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INTRODUCTORY QUALITATIVE ANALYSIS

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INTRODUCTORY QUALITATIVE ANALYSIS

BY

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PREFACE

Within recent times the selection of subject matter to be included in texts of qualitative analysis has become increasingly difficult. The time allotted for beginning courses has decreased until in many cases all that remains is the laboratory time of the second semester of the first year in chemistry, or even less. This diminution of time has been paralleled by a prodigious increase in the chemical knowledge which might with advantage be included in such a course. But with the decrease in the time allotted and the increase in subject matter, student capacity to learn remains much the same.

In choosing subject matter to meet the new conditions the teacher is confronted with a dilemma. If, on the one hand, enough experimentation is included to constitute a fair beginning, no time remains for consideration of other aspects, and the work may degenerate into mechanical execution of printed directions. If, on the other hand, sufficient time is taken to introduce even the simpler theories involved, the experimental part of the course suffers. The authors have as their purpose in this book the organization and presentation of a quantity of subject matter, fairly proportioned between experiment and theory, comprehensible to most second semester freshmen, and capable of being presented in approximately one hundred clock hours or less of laboratory time.

The effective use of the student's laboratory time requires that the work be planned to eliminate profitless efforts and to lead directly from the student's initial chemical understanding to certain definite objectives. In the experience of the authors much time has been lost in doing "preliminary experiments" which in the student minds were often only a series of isolated experiences. Much time has been lost in learning to understand the text sufficiently well to execute the directions. Another source of loss of time and attention is experimental methods which are poor in the hands of beginning students. Laboratory methods for freshmen should be as nearly "freshman proof" as possible.

Besides effectively acquainting the student with the scheme

of analysis, the qualitative analysis course should help the student gain an insight into the nature of chemical reactions. This objective is hardest of attainment. Directions can be given as to what is to take place on the laboratory desk with a fair expectation of predicting what will happen when the student executes the directions. But prediction is well-nigh impossible with regard to what will transpire in the student's mind when he observes a reaction. Yet at the end of the course that which has taken place in the student's mind is the only thing of much importance. For these reasons the planning of the theoretical matter is of primary importance. It is a matter of opinion with the authors that the acquisition of theoretical insight is not a result of simple volition, of persistent effort, or of memory on the part of the student. It has its genesis in an inquiring intellectual attitude, and is fostered by the consideration of experimental facts, the asking of stimulating questions by the instructor, and a continued exposure to chemical experience. In brief the items considered helpful in teaching qualitative analysis and important in organizing a text book on the subject are:

1. The effective organization of the experimental work.

2. The writing of directions so that students can read and successfully execute them with a minimum of interpretation by the instructor.

3. To introduce material and questions that will cause the student to think about chemical reactions.

It has been considered important that the student get a comprehension of the scheme of analysis as a whole as early in the course as possible. A series of exercises is given with this in view. The student first performs an experiment which shows how separations can be made by selective precipitation. Then he is given a solution containing most, but not all, of the twenty-three metallic ions included in the scheme of analysis. The first task is to separate the ions of this "practice solution" into the five groups of qualitative analysis. Then each of the groups so obtained is analysed.

When the analysis of the practice solution is completed, the student learns to test for the negative ions. Then he is ready for the analysis of an unknown material. This is given in the form of a mixture of two or three solid salts. At this point the dissolving of solids as a preliminary to analysis is taken up.

Students of fair ability will require about thirty clock hours for the execution of the laboratory work thus far described. The arrangement of the remainder of the work is left to the instructor in charge of the course. More unknowns may be given. These may be salt mixtures like the first, or a variety of other materials such as alloys, cement, clay, talcum powder or ceramic materials. They must not contain phosphates, however. Supplementary instructions may be needed in some cases.

For the attainment of the second objective mentioned above the authors have been careful in their use of the English language and have tried to resist the temptation to include too much. It will help if the students can be induced to read the directions before attempting the experiment. Supplementing the printed directions, outlines have been used for the graphic representation of analytical procedures. The device used is not original with the authors, but has been used at the State University of Iowa for some time. Its authorship is unknown.

The plan for acquainting the student with chemical theories and their application to the reactions encountered assumes that these theories have been presented in the course in general chemistry, but that further illustrations, applications, and amplifications will contribute to their better understanding. Along with the directions for the analysis of each group is given a discussion of the more important reactions involved. This is followed at the end of each chapter by a list of questions which serve both as a drill in procedure and as a basis of discussion of chemical theory. In the earlier chapters the intention is to raise questions rather than to settle them. If the student is made aware that certain facts need explanation, his interest will be increased when the explanation is presented.

The last four chapters are devoted to solubility product theory, chemical equilibrium and the theory of oxidation and reduction, as they apply to qualitative analysis. These are presented after the student has acquired some familiarity with reactions and has become aware of the necessity for attempting to answer more fully some of the questions raised earlier in the course. It is intended that instructors should use part of the laboratory time for class room discussion of these chapters. The ideas and terminology of the theory of ionization are used throughout.

Many details necessary for carrying out a fine analysis have

been omitted. Too many details in a beginning course tend to intellectual bewilderment and obscure more important objectives. Therefore, unknowns must have the constituents present in fairly large amounts, and the students should not be expected to correctly detect traces.

No provision has been made for the detection of strontium ion or phosphate ion, or for avoiding the complications introduced in the analysis by the presence of the latter. Strontium ion is not of enough practical importance to warrant its inclusion. The complications introduced by the presence of phosphate ion would require an undue proportion of the limited time available. For a similar reason the number of negative ions for which tests are given is limited.

No specific acknowledgments of the sources of the materials used in the book have been made. The materials, gathered from many sources, have been modified in the light of the experience of the authors so that adequate acknowledgment of the original sources is extremely difficult.

In conclusion, the authors wish to state that they are aware of the fact that this book imperfectly attains the objectives outlined, but if experience indicates that progress has been made they will feel themselves repaid for the effort expended.

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IOWA CITY, IOWA.
August, 1928.

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INTRODUCTORY QUALITATIVE ANALYSIS

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CHAPTER I

GENERAL INFORMATION

When the study of Qualitative Analysis is started at the beginning of a semester, part at least of the first laboratory period is usually devoted to the assignment of laboratory desks and the obtaining of apparatus and to other details incident to getting started. Also certain information is indicated below which it is well that the student acquire at this time.

1. Desk and Locker Assignments. Apparatus. General Information. Information as to how to obtain a laboratory desk assignment may be obtained from the Instructor in charge of the laboratory. A set of the necessary apparatus must be obtained also, if it is not already in the desk. A list of the articles needed is to be found in the appendix of this book, page 147.

There are certain other items about which the beginner in laboratory work needs to be informed. Most of the remainder of this chapter is devoted to certain of these. In addition those in the following list are worthy of mention:

1. How to obtain chemicals and apparatus.
2. Disposal of wraps during laboratory hours.
3. Location of drinking water and toilets.
4. Where to receive first aid in case of accident.
5. What to do in case of fire.
6. Lost and found articles.

2. Laboratory Accidents. Laboratory accidents are infrequent, but because they happen sometimes and because the difference of a few seconds in doing the right thing after an accident may make the difference between a trivial incident and a serious injury the following suggestions are offered. There are three types of laboratory accidents which may result seriously: accidents from fire, from corrosive chemicals, and fainting.

(*a*) *Fire.* A vessel containing an inflammable substance may be upset and become ignited, resulting in a fire on the desk or even the clothing of those standing near. A small fire is sometimes easily blown out. A larger fire may often be quenched by mopping with a towel. A still larger fire had best be attacked with a fire extinguisher. One should be located in every laboratory. Some laboratories have a shower bath or other provision for extinguishing fires on clothing. This should be investigated.

(*b*) *Chemicals.* Corrosive chemicals often get on the clothing or skin and if care is not taken damage may result. As a measure of precaution it is a good idea to mop up with a wet sponge immediately any chemicals that are spilled on the desk or on the floor. Even so apparently mild a substance as copper sulfate will make a hole in leather if left there a while. Whenever a corrosive substance gets on the skin the first measure to be taken is to wash it freely with water. If the skin continues to smart ask the Instructor what to do next. Or, if you have studied chemistry long enough to know the difference, apply sodium carbonate solution to acid burns and dilute acetic acid to sodium peroxide or base burns. The acetic acid on the side shelf is too concentrated. Do not put it on the skin without diluting with about 10 volumes of water.

Chemicals in the eye require special mention. When a person gets a chemical in the eye he may be so blinded as to be unable to help himself. Do not hesitate to lead such a person to the sink and slop copious quantities of water into the eyes. If the chemical is a strong one like concentrated sulfuric acid, place the person under the water tap face up and open the tap. Prompt action here may save a person from blindness. Do not put anything in the eye except water. If the eye still smarts or burns after the first treatment a drop of castor oil in the eye will often bring relief.

(*c*) *Breathing Irritating Gases.* Accidents sometimes occur which make it necessary to breathe irritating gases for longer or shorter periods. Breathing through a moist or even dry handkerchief or towel will often lessen the irritation. After the accident, if fresh air does not relieve the irritation in the nasal passages, try smelling denatured alcohol. If this does not bring relief, try *cautiously* smelling 6 *M* ammonium hydroxide.

(*d*) *Fainting.* People occasionally faint in the laboratory as

well as elsewhere. In the laboratory the chief danger arises from the possibility of striking the head against the sink or concrete floor in falling. A person who has fainted should be placed flat on the back wherever he is and let alone for as much as five minutes, after which time restorative measures may be employed. If you feel yourself fainting in time, tell your neighbor and lay yourself flat on the floor or a clean desk top, assisted by your neighbor. If you see one of your neighbors turn pale and begin to totter, assist him to lay himself out flat on his back, avoiding contacts between head and stone desk tops on the way down.

3. Ventilation. (*a*) *Polluted Air.* The air in laboratories devoted to qualitative analysis sometimes becomes badly polluted. Breathing such air may contribute to or cause fainting, headaches, dizziness, colds, bronchitis, or mental and physical fatigue at the conclusion of the laboratory period. Instructors and students should cooperate in trying to keep the laboratory a healthy place in which to work.

Laboratories should be maintained at a relatively low temperature. The quantity of heat generated by the use of a large number of bunsen burners is surprising, as is also the quantity of pollution contributed by the gaseous products of combustion. Turning down or extinguishing burners when not in use minimizes pollution.

(*b*) *Fumes.* Laboratory directions for Qualitative Analysis often require that solutions containing acids or ammonium salts be evaporated to a smaller volume or to dryness, with the result that quantities of corrosive vapors are liberated. Such an evaporation should be conducted so that fumes are not liberated in the room, that is, before a fume duct or in a hood. Fume ducts or hoods are of little use if the fans or other mechanical ventilating devices are not in operation. Report to your Instructor whenever the ventilating devices fail to remove the fumes. Also remonstrate with your neighbors whenever they do anything to pollute the air of the laboratory.

(*c*) *Hydrogen Sulfide.* Another source of pollution of laboratory air is hydrogen sulfide gas. This gas, which is necessarily much used in Qualitative Analysis, is a dangerous poison. Breathing it in high concentration will cause death in ten minutes or less. Its concentration in the air in the laboratory never

gets high, but even in low concentrations it contributes to or causes many of the physiological effects of breathing bad air previously mentioned. The one precaution in the use of hydrogen sulfide is to use it in such a way that little escapes into the air of the room. It is a good idea to have a nearby window open while using hydrogen sulfide. Fresh air is the best antidote for hydrogen sulfide poisoning.

4. Miscellaneous Suggestions and Directions. Burned matches, broken glass, used filters, and other solid waste material should not be placed in the sink unless you wish to flood the laboratory. Such materials should be placed in waste jars. The waste jar may be placed at some distance from where you work and running to it each time you use a match may be inconvenient. It is suggested that while doing laboratory work you keep a beaker or other vessel on your desk and in it place all the solid waste during the laboratory period. At the end of the period make a trip to the waste jar and empty it.

Many steps can be saved in using reagents located on side shelves. There are two ways in which a portion of a reagent can be transported from the side shelf to your desk. You can take a vessel, go to the side shelf, pour out the required quantity of reagent, and return to your desk, walking twice the distance from your desk to the side shelf. Or, you can go to the side shelf, bring the reagent bottle to your desk, use it and return it to the side shelf, walking four times the distance between your desk and the side shelf. The latter method will not only take extra steps and time, but will inconvenience others who need to use the same reagent.

When heating a solution in a test tube do not aim the opening toward yourself or toward a neighbor.

When mixing two liquids, particularly when one of them is concentrated sulfuric acid, always pour the heavier into the lighter, thus lessening the chance for spattering.

When too much of a solid or liquid has been poured from a reagent bottle, never pour the excess back into the bottle. Either save it till you need it or throw it away. This lessens the chance of introducing impurities into the reagent.

While a material is being removed from a reagent bottle, do not lay the stopper down in such a manner that the part of the stopper which enters the neck of the bottle comes in contact with

the desk top. Replace stoppers when through using reagent bottles.

EXERCISE 1

Make two wash bottles, a precipitation flask and a trap. Make one of the wash bottles from a Florence flask of 500 cc. to 1 liter capacity as shown in Fig. 1*a*. Make the other wash bottle and the precipitation flask from Erlenmeyer (conical) flasks of about 250 cc. capacity, as shown in Fig. 1*b* and Fig. 1*c*, respectively. The trap can be made from a wide mouth bottle of a capacity of 100 cc. or more, as shown in Fig. 1*d*. Use rubber stoppers. See that each stopper fits the opening for which it is intended before inserting the glass tubing.

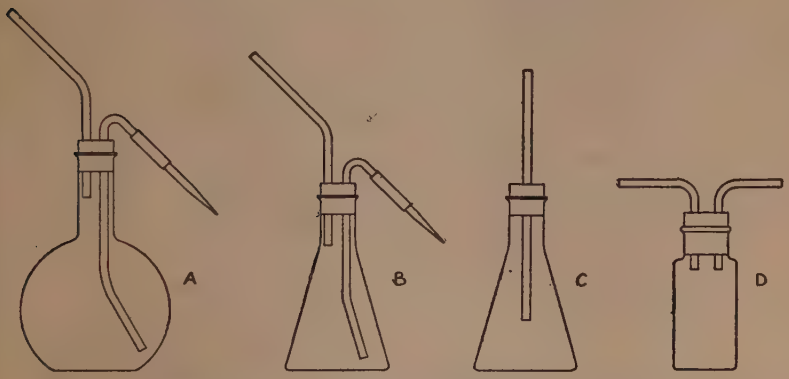


FIG. 1. *A*. Wash bottle for distilled water, 500 cc. to 1000 cc. capacity. *B*. Wash bottle for various wash solutions, 250 cc. capacity. *C*. Precipitation flask, 250 cc. capacity. *D*. Trap for suction filter, 100 cc. or larger. The inlet and outlet tubes should have an outside diameter of 7 mm. or more.

After the various pieces of glass tubing have been bent to the desired shapes and cut to the right lengths, the ends should be fire polished, that is, held in the flame till the edges of the glass begin to soften. After this allow the glass to cool. Fire polishing is important, not only because fire polished tubes are more easily thrust through rubber stoppers, but also because there is much less danger of cutting oneself or the rubber in the process.

Before starting to push a glass tube through the hole of a stopper, wet the tube and the inside of the hole. When pushing the tube through, *take hold of the tube near the stopper*. This will greatly reduce the danger of the tube breaking and cutting your hand.

The larger wash bottle is to be used only for distilled water. Whenever the directions in the book call for the use of water, distilled water should be used. The smaller wash bottle is to be used for specially prepared wash solutions. The precipitation flask is to be used when

precipitation by hydrogen sulfide gas is required. The trap is to be used in connection with a suction filter, as explained in Chapter II, page 16.

When the wash bottles and the precipitation flask are finished, make three stirring rods, each 15 to 18 cm. (6 to 7 inches) long. These are merely solid glass rods with the ends fire polished.

CHAPTER II

SEPARATION OF THE COMMON METALLIC IONS INTO GROUPS

Qualitative analysis consists of the separation of a complex substance or mixture into its constituents and the identification of the constituents. For example, by means of qualitative analysis it is possible to learn what things are present in a dime, a brick, or a glass window pane. The word qualitative signifies that the object of the analysis is merely to identify the constituents of the compound or mixture with no attempt to determine their amounts. If the quantities of the constituents are determined the process is called quantitative analysis. The following exercise will serve as an introduction to the study of qualitative analysis.

EXERCISE 2

Separation by Precipitation

The object of Exercise 2 is to show how two metallic ions in a solution can be separated from each other and from the solution.

Mix together in an Erlenmeyer (or conical) flask 5 cc. of silver nitrate solution and 2 cc. of copper nitrate solution. Dilute the solution with about 25 cc. of distilled water.

The silver ion can be removed from the solution in the following manner. Add slowly, with constant shaking, 2 cc. of 6 *M* hydrochloric acid. Observe what happens. Shake the flask till the precipitate coagulates and settles quickly to the bottom when the shaking is stopped. The precipitate is next separated from the solution by filtration, which is accomplished in the following manner. Take a circular filter paper, *A* in Fig. 2, and fold it along a diameter as indicated by the dotted line, obtaining *B*. Fold *B* along the dotted line, obtaining *C*. Open one side of the folded paper as indicated in *D*, obtaining a folded paper that will fit snugly in the glass funnel *E*. Put it in the funnel and wet it with distilled water. Support the funnel in the top of an Erlenmeyer flask. Pour into the filter as much clear solution as possible without having the liquid on the filter rise above the edge of the filter paper. After most of the clear solution has been filtered, pour the rest of the solution and the precipitate into the filter. The time required for filtration will generally be shortened if most of the clear solution is poured off and filtered before much of the

solid precipitate is allowed to get on the filter. This manner of pouring off the solution without disturbing the precipitate is often called "decantation." The solution that has passed through the filter into the flask under the funnel is called the "filtrate."

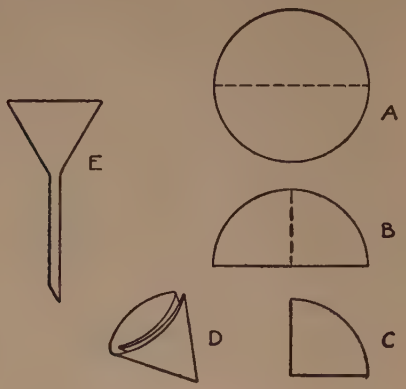


Fig. 2. Making a filter.

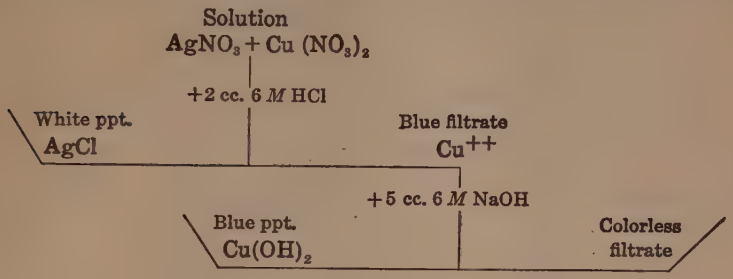
When filtration is complete, replace the flask containing the filtrate by an empty one and wash the precipitate by playing on it a stream of water from the wash bottle, letting the water run through the filter. The wash water can be thrown away. Note the color of the precipitate and the filtrate. Where are the silver and copper? How can you tell?

Now add 5 cc. of 6 *M* sodium hydroxide to the filtrate and mix well. What do you observe? Filter part of the mixture, using a fresh filter paper, and note the color of the precipitate and filtrate. Where is the copper? Has the copper been separated from the solution? Write the answers to these questions in your notebook. Separations like this one are the basis of qualitative analysis.

5. Recording Qualitative Analysis Procedure. In connection with the directions given below, a diagrammatic or outline method for recording the processes of qualitative analysis is used. This method is useful both in giving laboratory directions and in stating experimental results. As an example, Outline 1 is given for the separation and precipitation of silver ion and copper ion as carried out in Exercise 2. It should be copied in the notebook to help in learning the scheme and as part of the record of Exercise 2.

The meaning of the outline can be read as follows. The original solution, which contained silver and copper nitrates, was treated with 2 cc. of 6 *M* hydrochloric acid. The mixture

was then filtered. Filtration is indicated by the junction of a vertical line with a horizontal line. The part of the horizontal line to the *left* of the junction always represents the *precipitate* (solid) and the part to the *right* always represents the *filtrate* (liquid). Whenever a mixture is filtered, both precipitate and filtrate must be accounted for. In this case the precipitate was



OUTLINE 1. Separation of silver and copper ions.

silver chloride. It was thrown away, or "rejected" as indicated by the end of the line being turned up. The filtrate was blue and contained the copper in the form of cupric ion. Sodium hydroxide solution was added to the filtrate and the mixture was filtered. The precipitate was blue and consisted of copper hydroxide. It was thrown away. The colorless filtrate was thrown away also.

The conventions for representing filtration and rejection and the indication of treatment other than filtration by a vertical line progressing in a downward direction should be adhered to carefully. On the other hand considerable latitude is permissible in what is noted down as observations, explanations and conclusions. There is one more convention not shown in the outline given. When a final test is made and a particular ion is found present, the record of the final test in the outline is enclosed in a square to call attention to it. If the ion in question is found to be absent, no square should be put around the record of the test.

6. The General Methods Used in Qualitative Analysis. In Exercise 2 a method was shown for separating silver and copper ions from each other when they were originally mixed in the same solution. Separation was possible by virtue of the fact that

silver ion will form a precipitate by uniting with chloride ion while copper ion will not. One ion possesses a property not possessed by the other. By an extension of this idea very complex substances may be separated into their constituent parts. Of course the larger the number of different substances composing a mixture the more complicated the matter of analysis becomes. In courses such as this, the number of substances that are to be sought in any one mixture is usually limited to twenty-five or less of the commonly occurring metallic ions and a smaller number of negative ions (acid radicals). Methods for the systematic analysis of positive ions are found in Chapters IV to VIII inclusive, and directions for the detection of negative ions are found in later chapters.

In an analysis of a solution which may contain any or all of twenty to twenty-five metallic ions, the first step is to separate the ions into five different groups. After this each group is analyzed separately for the individual ions which it contains. Exercise 3 in this chapter is an exercise in separation of the groups, while Exercises 4 to 8 in Chapter III are exercises in the analysis of group precipitates. Directions for these exercises are given both in outline form and in the printed text. The latter should be followed rather than the former while the work is being done, as many details not given in the outlines are given in the text. The outlines will serve in giving an idea of the process as a whole and should be consulted frequently during the work.

It is to be noted that in each of the outlines most of the filtrates and precipitates are numbered. For example, in Outline 2, p. 12, hydrochloric acid is added to the original solution and a precipitate is formed. The precipitate is numbered (1) and the filtrate is numbered (2). The filtrate is treated with hydrogen sulfide and another precipitate is formed which is numbered (3), while the filtrate from precipitate (3) is numbered (4), and so on. The purpose of the numbers is to aid in identifying filtrates and precipitates. When a precipitate or filtrate is to be set aside, even if only for a short time, it should be labelled for later identification. Marking the container with the number of the corresponding precipitate or filtrate in the outline is a convenient method of labelling.

EXERCISE 3

Separation of the Metallic Ions into Groups

(*a*) *Object.* Obtain 20 cc. of a practice solution from your instructor. It will contain most but not all of the following twenty-three ions: lead, mercurous, silver, mercuric, bismuth, copper, cadmium, arsenious, antimonous, tin, aluminum, chromium, zinc, manganese, iron, nickel, cobalt, barium, calcium, magnesium, sodium, potassium, and ammonium. The object of the exercise is to separate the ions present in the 20 cc. of practice solution into the groups indicated in the following list:

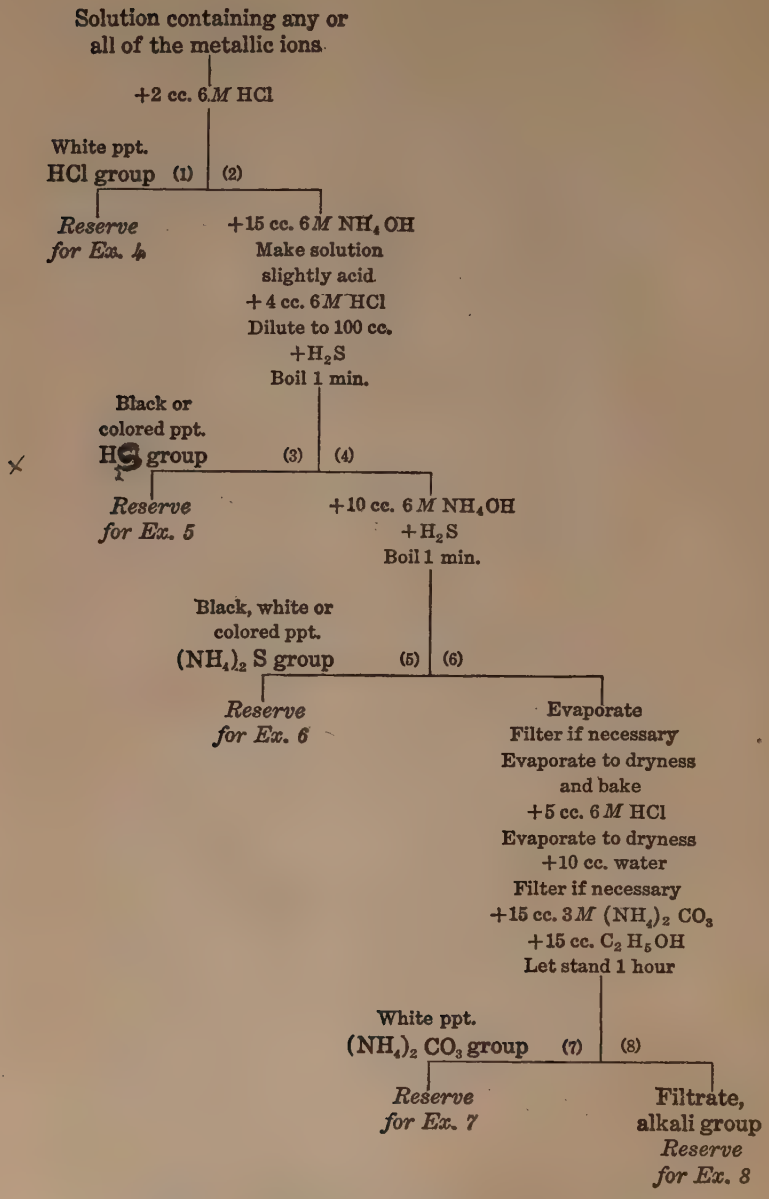
HCl Group	H_2S Group	$(NH_4)_2S$ Group	$(NH_4)_2CO_3$ Group	Alkali Group
Pb^{++}	Hg^{++}	Ni^{++}	Ba^{++}	Na^{+}
Hg^{+}	Pb^{++}	Co^{++}	Ca^{++}	K^{+}
Ag^{+}	Bi^{+++}	Zn^{++}	Mg^{++}	NH_4^{+}
	Cu^{++}	Mn^{++}		
	Cd^{++}	Fe^{++}		
	As^{+++}	Al^{+++}		
	Sb^{+++}	Cr^{+++}		
	Sn^{++}			

This may be done by carefully following the directions given below. The method to be used is shown in Outline 2.

(*b*) *Precipitation of the Hydrochloric Acid Group.* Put 20 cc. of practice solution into an Erlenmeyer flask and add to it 2 cc. of 6 *M* hydrochloric acid. If any of the ions of the hydrochloric acid group are present, they will be precipitated as chlorides. If there is no precipitate, none of the group is present, except possibly a small amount of lead ion. If no precipitate has formed, filtration is not necessary, and the directions in the next paragraphs can be skipped for the present. The solution should then be treated for the precipitation of the hydrogen sulfide group (Section *f*.) If there is a precipitate it must be filtered out as directed in the next paragraph.

(*c*) *Filtering.* Prepare a filter as described on page 8. Let the precipitate settle and decant the clear solution into the filter. Then pour the precipitate into the filter. If a portion of the precipitate sticks to the inside walls of the flask it may be washed out into the filter by means of a 2 *M* hydrochloric acid solution, prepared by mixing 30 cc. of water with 15 cc. 6 *M* hydrochloric acid in the small wash bottle. This 2 *M* hydrochloric acid will also serve as a wash solution for the precipitate.

(*d*) *Washing the Precipitate.* When all the precipitate has been transferred to the filter, and the solution has passed through the filter, remove the flask containing the filtrate and substitute another. Wash the precipitate once with 2 *M* hydrochloric acid solution as follows. Direct a stream from the wash bottle upon the edge of the filter paper. When all the precipitate has been wet by the wash



OUTLINE 2. Separation of the metallic ions into groups.

solution, allow all the wash solution to run through. If a precipitate is to be washed more than once, all of the previous wash solution should be allowed to pass through the filter before more is added.

The reason for washing precipitates after filtration is to free them from the liquid in which they were formed, often called "mother liquor." The mother liquor nearly always contains substances that might interfere with the later tests for the metals in the precipitate. Hence washing the precipitate should not be omitted. Wash solutions after use may be thrown away, although ordinarily no harm is done if they are added to the filtrate.

(*e*) *Preserving Precipitate and Filtrate for Future Use.* Next remove from the funnel the paper containing the hydrochloric acid group precipitate, roll it up, and put it into a bottle or test tube, which should contain a few drops of water to keep the precipitate from drying out. Cork the test tube tightly, label it (1), and set it aside till the precipitate is to be analyzed in Exercise 4. The number (1) refers to the same number in Outline 2, and will serve to identify the precipitate later.

The filtrate from the hydrochloric acid group contains the other four groups. If a solution like this one is to stand for any length of time before it is used, for instance till the next laboratory period, the flask containing it should be carefully corked and labelled. This filtrate can be labelled (2). Number (2) can be found from Outline 2 to mean the filtrate from the hydrochloric acid group.

(*f*) *Precipitation of the Hydrogen Sulfide Group.* Successful precipitation of the hydrogen sulfide group requires care in regulating the quantity of acid present in the solution. Trouble will follow if either too much or too little hydrochloric acid is present during the addition of hydrogen sulfide.

The hydrogen sulfide group is precipitated from the filtrate from the hydrochloric acid group. Add 15 cc. of 6 *M* ammonium hydroxide and shake well. If the solution is not basic to litmus, continue the addition of 6 *M* ammonium hydroxide, 1 cc. at a time, till the solution after shaking is basic. The addition of ammonium hydroxide may cause the formation of a precipitate, but this may be ignored. Then add 6 *M* hydrochloric acid 1 cc. at a time till the solution is acid to litmus. Finally add just 4 cc. of 6 *M* hydrochloric acid in excess. If there should be a colored precipitate left after the addition of the acid, heat till it dissolves. A white precipitate will do no harm. Dilute the solution to 100 cc. with distilled water, ignoring any precipitate that is formed, and put it into the precipitation flask made in Exercise 2.

Connect the glass tube of the precipitation flask to a source of hydrogen sulfide gas and pass hydrogen sulfide into the flask for a few seconds with the stopper loose so that air can escape. When enough gas has been passed in to expel the air in the flask, put the stopper in tight and shake the flask vigorously and continuously to hasten the

absorption of the gas by the solution. Continue the addition of hydrogen sulfide gas till the solution is saturated.[1]

There are various ways of telling when the solution is saturated with hydrogen sulfide. Perhaps the following is as simple as any. Remove the stopper of the precipitation flask and place the thumb or fleshy part of the palm of the hand over the outlet of the flask and shake. If the solution is saturated a slight increase of pressure in the flask will be noticed. If the solution is not saturated, a slight decrease of pressure in the flask will be noticed. Saturation is indicated also if the precipitate settles readily and leaves a clear solution above it. However, a solution may be saturated and not show this test.

If no precipitate is formed, absence of all the ions of the hydrogen sulfide group is indicated. In such a case pass directly to the ammonium sulfide group (Section *g*) treating the solution as if it were the filtrate from the hydrogen sulfide group. Sometimes a precipitate of sulfur and nothing else is formed. This can be recognized by its light cream color and the fact that some of it goes through a filter. In this case the solution should be boiled to coagulate the sulfur, then filtered and the precipitate rejected. The filtrate can then be treated for the ammonium sulfide group.

The presence of ions of the hydrogen sulfide group is indicated by a black or colored (not white) precipitate. If there is a black or colored precipitate, gently boil the solution for about one minute. Next allow the precipitate to settle for a minute or two, then filter. Use decantation as much as possible as this will save time.

When filtration is complete, the filtrate should be tested to make sure that the hydrogen sulfide group was completely precipitated. Heat the filtrate to boiling and add hydrogen sulfide as before. Absence of a precipitate indicates that precipitation was complete, and the solution can be used for the precipitation of the ammonium sulfide group. If there is a further precipitate, add enough hydrogen sulfide to saturate the solution, then filter as directed above and add the precipitate to the former hydrogen sulfide precipitate. Repeat till no black or colored precipitate is formed when hydrogen sulfide is passed into the filtrate. Save the filtrate for the precipitation of the ammonium sulfide group, labelling the container (4) if the solution is not to be used immediately.

Wash the hydrogen sulfide group precipitate three times with water to which hydrogen sulfide has been added. Use the small wash bottle for this. Put water in it and bubble hydrogen sulfide gas through for a short time, shaking vigorously. Directions for washing a precipitate can be found in Section *d* above. It should be noted, however, that

[1] **Caution.** When using hydrogen sulfide remember that it is an actively poisonous gas. It will cause headaches even if breathed in low concentrations. However, its effects are immediate; that is, breathing it today will not affect one tomorrow. It is well to have a window at least partly open near the source of hydrogen sulfide gas and to avoid as far as possible getting any quantity of it in the air of the room.

this precipitate is to be washed with a hydrogen sulfide solution rather than with a hydrochloric acid solution.

When the precipitate is washed, make a hole in the filter paper and wash the precipitate into a test tube by means of a stream from the small wash bottle. If it is necessary to use more water than the test tube will hold, the precipitate can be allowed to settle and some of the water can be thrown away. Cork the test tube, label it (3) and set it aside along with the hydrochloric acid group precipitate for use in Exercise 5.

(*g*) *Precipitation of the Ammonium Sulfide Group.* The ammonium sulfide group is to be precipitated from the filtrate from the hydrogen sulfide group. Ammonium sulfide is the reagent for this group. However, instead of adding an ammonium sulfide solution, the reagent is formed by adding both ammonium hydroxide and hydrogen sulfide which react to form ammonium sulfide.

$$2\ NH_4OH + H_2S \rightarrow (NH_4)_2S + 2\ H_2O \qquad (1)$$

The filtrate from the hydrogen sulfide group must first be neutralized with ammonium hydroxide, and then a small excess of the latter must be added. Then the basic solution is saturated with hydrogen sulfide.

To precipitate the ammonium sulfide group add 10 cc. of 6 *M* ammonium hydroxide to the filtrate from the hydrogen sulfide group and shake the solution. If it is not basic to litmus continue the addition of ammonium hydroxide in 5 cc. portions till the solution is basic. The formation of a precipitate as the solution becomes basic is to be expected if the solution contains hydrogen sulfide and any of the ions of the ammonium sulfide group, or even in the absence of hydrogen sulfide if aluminum, ferric or chromium ion is present.

The solution is now in condition for the addition of the hydrogen sulfide. Pass in hydrogen sulfide gas as in the precipitation of the hydrogen sulfide group, till after a thorough shaking of the flask the gas inside will darken filter paper moistened with lead nitrate solution. If there is no precipitate, pass on the ammonium carbonate group, treating the solution as if it were the filtrate from the ammonium sulfide group.

If there is a precipitate when the solution is saturated with hydrogen sulfide, boil the solution for one minute. Then test with litmus. If the solution is not basic, add 6 *M* ammonium hydroxide in 2 cc. portions till it is basic and filter. If the amount of precipitate is not large, filter as described for the filtration of the hydrogen sulfide group. Wash with a very dilute ammonium sulfide solution prepared by passing hydrogen sulfide into a solution containing 1 or 2 cc. of 6 *M* ammonium hydroxide to 100 cc. of water. If the amount of precipitate is large, it will be advantageous to filter and wash by suction as described below. In either case the wash water can be thrown away.

When filtration is complete, the filtrate should be tested to make sure that the ions of the ammonium sulfide group are completely

precipitated. To do this, place the filtrate in the precipitation flask and treat with hydrogen sulfide as before. Absence of a precipitate indicates that precipitation was complete. If the second addition of hydrogen sulfide causes further precipitation, saturate the solution with hydrogen sulfide, boil, and filter. Repeat this process of testing the filtrate for completeness of precipitation till the addition of hydrogen sulfide to the filtrate no longer causes a precipitate to form.

Join all the precipitates that are formed by the successive treatments with hydrogen sulfide, washing them into a test tube as described for the hydrogen sulfide group. Cork the tube, label it (5), and save it for future analysis in Exercise 6. Save the filtrate, as it still contains the ammonium carbonate group and the alkali group. The filtrate can be labelled (6).

(*h*) *Filtering by Suction.* Precipitates which will clog an ordinary filter, making filtration slow, can be filtered more quickly by means of a suction filter. A suction filter is a device for applying suction to the lower end of a filter. One type of apparatus for this purpose is shown

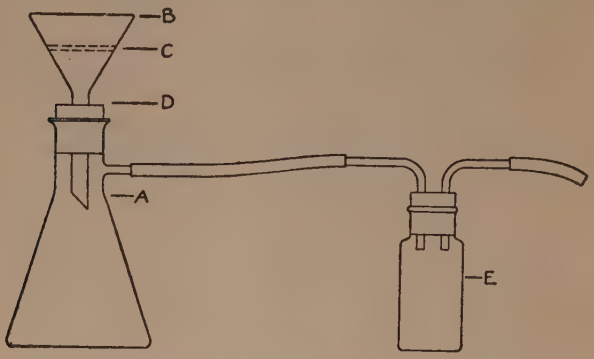


Fig. 3. Suction filter and trap.

in Fig. 3. It consists of a thick-walled flask *A*, called a filter flask, having a side arm for connecting to the suction and a porcelain funnel *B*, sometimes called a Hirsch funnel, with a perforated diaphragm at *C*. The stem of the Hirsch funnel is put through a hole in the rubber stopper *D* which fits tightly in the neck of the flask. The suction or partial vacuum, is usually produced by a so-called filter pump operated by water power. The filter pump can be attached to a water faucet and is connected to the filter flask by means of a rubber tube.

A trap of some sort should be connected in series between the filter flask and the filter pump. This lessens the chance of liquids passing in either direction between the pump and the flask. A satisfactory trap may be made by fitting a small wide mouth bottle with a two-hole rubber stopper bearing outlet and inlet tubes of glass as shown in Fig. 1 and *E* of Fig. 3. When this trap is placed in series between the

flask and the pump any liquids passing in either direction will be retained in the bottle.

To prepare a suction filter, assemble the apparatus as shown in Fig. 3, connecting the filter flask to the trap and the trap to the filter pump by rubber tubing. Place on the diaphragm of the funnel a piece of filter paper that is slightly smaller than the diaphragm, but which covers all the holes. Wet the filter paper and turn on the suction. Now pour some water on the filter to see that there are no leaks and that the filter is working satisfactorily. Press down with the finger any portions of the paper which are not tight against the diaphragm. If the filter seems to work satisfactorily, break the suction, best by pulling the rubber tube off the side arm of the filter flask, and pour the water out of the flask. Reassemble the apparatus, apply the suction, and proceed with the filtration much as with an ordinary filter. The same directions for washing apply to a precipitate on a suction filter as apply to a precipitate on an ordinary filter. At the end of a filtration break the suction before turning off the filter pump.

Fine-grained precipitates are sometimes drawn through a suction filter. When this happens, the filtrate may be poured through the filter a second time. Usually enough of the precipitate is retained in the first filtration to make a filter bed that will hold a finer precipitate than will the filter paper alone. Sometimes only a small amount of precipitate passes through, and time can be saved by refiltering through an ordinary folded paper without suction and throwing away the small precipitate.

(*i*) *Precipitation of the Ammonium Carbonate Group.* The filtrate from the ammonium sulfide group contains the ions of the ammonium carbonate and alkali groups. It will also contain considerable quantities of ammonium salts, and various sulfur compounds. Also it may contain small quantities of ions of metals of the hydrogen sulfide group or ammonium sulfide group which faulty manipulation has failed to remove. It is desirable to remove all of the three last mentioned classes of materials before attempting to precipitate the ammonium carbonate group. To do this, place the filtrate from the ammonium sulfide group in a beaker. Then begin to evaporate the solution to dryness. Oftentimes a precipitate will appear before the solution is half evaporated. This may be free sulfur resulting from decomposition of the sulfur compounds present, or a mixture of sulfur and sulfides of metals of previous groups. In any case continue the boiling till the precipitate is coagulated sufficiently to be readily removed by filtration. Then filter, reject the precipitate, and continue the evaporation of the filtrate. When the volume of the solution has been reduced to 50 cc. or less, transfer the solution to a casserole or evaporating dish of about 75 cc. capacity, after which continue the evaporation. Just before the contents of the casserole become dry they often tend to spatter. When this happens, remove the flame till spattering ceases. Place the casserole on a triangle supported on a

ring stand and in a position where the top of the casserole is as high as the opening in the fume duct and not more than one inch away. (If fume ducts are not available use a hood.) This is to avoid polluting the laboratory with fumes of sublimed ammonium salts which are copiously given off during the remainder of the process.

Continue heating carefully, increasing the heat when spattering ceases and finally heat till the smoke of ammonium salts stops coming off. If desired, the burner can be inverted and the mass can be heated from the top. This will minimize spattering and make the process more rapid. The process of evaporating the liquid of a solution and then heating the residue is sometimes implied by the words "evaporate to dryness and bake."

When the filtrate from the ammonium sulfide group has been evaporated to dryness and baked, all of the ammonium salts and the sulfur will have been removed. Ions of metals incompletely removed in the precipitation of previous groups may or may not be present in the residue. A method for judging this matter is mentioned below.

Allow the casserole to cool enough so that it will not be cracked by contact with cool liquids. Then add 5 cc. of 6 *M* hydrochloric acid and heat. If a solid residue adheres to the casserole rub it loose with a stirring rod. Evaporate till spattering begins or to dryness if the quantity of residue is small.

At this point examine the residue in the casserole. If there is no residue left, ions of the carbonate and alkali groups are absent, and the separation into groups is finished.

If the residue is any color other than clean white, ions of the ammonium sulfide group are probably present, and the task of precipitating this group must be repeated. To do this, dissolve the residue in 5 cc. of 6 *M* hydrochloric acid and some water. When the solid residue is dissolved, treat the resulting solution as a filtrate from the hydrogen sulfide group.

If the residue is white, any or all of the ions of the carbonate and alkali groups may be present. Dissolve the residue in 10 cc. of water. If necessary stir and warm the mixture to hasten the dissolving process. Filter out and reject any insoluble residue. Treat the solution as described in the next paragraph.

To the clear solution, which should not exceed 10 cc. in volume, add 15 cc. of 3 *M* ammonium carbonate and 15 cc. of alcohol (C_2H_5OH). Let the mixture stand, with frequent shaking, for at least one hour before proceeding.

Absence of a precipitate shows the absence of the ammonium carbonate group in the original solution. In this case label the solution (8) and set it aside till the alkali metals are to be tested for.

If there is a precipitate, filter it out. Label the filtrate (8) and set it aside till it can be tested for the alkali metal ions. Examine the flask in which the precipitation was made to see if an appreciable amount of the precipitate is sticking to the sides. If so it will be of advantage to put the rest of the precipitate in the same flask to

preserve it. Transfer the filter paper with the precipitate on it to the vessel in which it is to be preserved and save the precipitate till it can be analyzed in Exercise 7. It can be labeled (7).

Electrolytes and Their Reactions

7. Acids. Practically all the substances met in inorganic qualitative analysis belong to the class of substances called electrolytes. Electrolytes are divided into three classes, acids, bases, and salts. Acids all have a sour taste and in water solution turn litmus paper red. The sourness of vinegar, unripe fruit, sour milk, and most other things sour to the taste is caused by the presence of acids. The formulas of acids, as ordinarily written, always begin with H; for example HCl, H_2SO_4, H_2S, HNO_3. Under ordinary conditions pure acids may exist as solids, liquids, or gases. With the exception of concentrated sulfuric acid, pure acids are seldom used in the laboratory, but instead water solutions of the acids are used. Most acids dissolve freely in water.

8. Bases. Sodium hydroxide, ammonium hydroxide, and slaked lime are examples of bases. Many bases can exist only in the presence of water and decompose when an attempt is made to dry them. Most bases are only slightly soluble in water, but potassium, sodium, and ammonium hydroxides are exceptions to this rule. Water solutions of bases turn litmus paper blue. The formulas of bases, as ordinarily written, end in OH; for example NaOH, $Ca(OH)_2$, $Al(OH)_3$, NH_4OH. The OH group is often called "hydroxyl" or "hydroxide," and bases are often called "hydroxides."

9. Salts. Salts are nearly always solids at ordinary temperatures and are generally crystalline in form. When the crystals are small, salts often appear to be powders. Table salt, baking soda, and marble are nearly pure salts. Glass, paint pigments, rocks, and soils are composed mainly of mixtures of salts. Different salts vary widely in color and solubility in water. A liter of water will dissolve 0.002 g. of silver chloride and 1219 g. of silver nitrate, a million times as much. Solutions of some salts turn litmus blue, others turn it red, and still others do not affect the color of litmus paper. There is no single element or group of elements found in all salts such as the hydrogen in acids or the hydroxyl group in bases.

10. Reactions. When two or more electrolytes are mixed in the same water solution, chemical reaction often occurs. Quali-

tative analysis is based on the reactions of electrolytes and a study of the reactions is an important part of the study of qualitative analysis.

The reactions employed in Exercise 3 for separating the ions into groups are all more or less alike with respect to the fact that in each case two electrolytes are mixed, chemical action ensues, and a precipitate containing a metallic ion is formed. For example, consider the reaction between hydrochloric acid and silver nitrate, which can be represented by the following equation

$$HCl + AgNO_3 \rightarrow HNO_3 + AgCl\downarrow \qquad (2)$$

This chemical equation expresses the fact that hydrochloric acid and silver nitrate when mixed form nitric acid and a silver chloride precipitate, the precipitation of the silver chloride being indicated by the downward-pointing arrow. The equation also gives the proportions by weight in which these substances react, but with this aspect we are not at present concerned.

11. Double Decomposition. A closer inspection of Equation 2 will make clearer what has happened in the reaction. At the beginning the hydrogen was associated with the chlorine and at the end it is associated with the nitrate radical. At the beginning the silver was associated with the nitrate radical and at the end it is associated with the chlorine. The hydrogen and the silver seem to have changed places, or to have changed partners. Reactions like this are called "double decompositions" and are very common among electrolytes. In a double decomposition the metallic parts of two electrolytes merely change partners.

12. Ionization. While the ideas implied in expressions such as Equation 2 are useful and true, a more detailed idea of just what happens during the reaction is obtained by using the ideas of the theory of ionization. According to this theory hydrochloric acid in water solution does not exist as molecules of the composition implied by the formula HCl, but exists largely or entirely in the form of positive hydrogen ions and negative chloride ions. A hydrogen ion is a hydrogen atom from which one electron (one unit of negative electricity) is missing, leaving it with a unit positive charge. It is indicated by the symbol H^+. A chloride ion is a chlorine atom to which one electron has been added, giving it a unit negative charge. A chloride ion is indicated by the symbol Cl^-.

13. Equations in the Ionic Form. Similarly a water solution of silver nitrate contains few if any molecules as implied by the formula $AgNO_3$, but does contain silver ion, indicated by Ag^+, and nitrate ion, indicated by NO_3^-. When solutions of hydrochloric acid and silver nitrate are brought together the dissolved substances are not HCl and $AgNO_3$. They are hydrogen ion, H^+, silver ion, Ag^+, chloride ion, Cl^-, and nitrate ion, NO_3^-. When these four kinds of ions have been mixed, it is found that only two kinds of ions have done anything chemically. The silver ion and the chloride ion have united to form solid silver chloride, leaving hydrogen ion and nitrate ion (not HNO_3 molecules) in solution. This ionic view of the reaction may be expressed by an equation.

$$H^+ + Cl^- + Ag^+ + NO_3^- \rightarrow AgCl\downarrow + H^+ + NO_3^- \qquad (3)$$

An inspection of Equation 3 shows that the essential part of the reaction can be expressed by a briefer equation.

$$Ag^+ + Cl^- \rightarrow AgCl\downarrow \qquad (4)$$

The hydrogen ion and the nitrate ion do not take part in the reaction any more than the water in which they are contained. Just the same precipitate would form if silver sulfate and sodium chloride solutions were mixed.

In the discussions that follow, equations in the form in which Equation 2 is written are called molecular equations, while equations in the form of Equation 3 or Equation 4 are called ionic equations. Both forms have their particular uses as well as their limitations in representing chemical reactions.

In balancing an ionic equation care should be taken that it is balanced not only with respect to the numbers of atoms on the two sides of the equation, but also with respect to the electrical charges. The algebraic sum of the charges on one side of the equation must be equal to the algebraic sum of the charges on the other side. It is not necessary that the algebraic sum of the charges on either side be zero, although this often happens to be the case. If an unbalanced charge appears, it is understood that one or more ions with an equal and opposite charge have been omitted from the equation. The nitrate ion alone, for example, might be omitted from both sides of Equation 3, leaving the charge of the hydrogen ion unbalanced.

14. Application of the Theory of Ionization to the Separationn of the Groups. The preceding discussion indicates that silver ion can be removed from a solution by allowing it to unite with chloride ion to form a precipitate of silver chloride, which can be filtered out. In general it may be stated that any ion can be removed from a solution if it will unite with some other kind of ion to form a precipitate. This is illustrated by the fact that in Exercise 3 the addition of hydrochloric acid solution precipitated lead, silver and mercurous ions from the solution. It is because the chlorides of lead, silver, and mercury are only slightly soluble in water that these precipitates are formed. The solution from which the lead, silver, and mercurous ions were precipitated contained other metallic ions such as copper ion, zinc ion, and iron ion, but these were not precipitated when hydrochloric acid solution was added, because copper, zinc, iron, and the other metallic ions do not form slightly soluble chlorides.

The separation of the other groups is similar. Sulfide ion in an acid solution precipitates only the hydrogen sulfide group, provided that the hydrochloric acid group has already been removed. Hydroxide ion and sulfide ion in a basic solution precipitate only the hydroxides or sulfides of the ammonium sulfide group, if the two preceding groups have been removed. Carbonate ion in a basic solution precipitates only the carbonate group, if the three preceding groups are absent.

15. Reactions Involved in the Separation of the Groups. The reactions involved in the separation of the groups are double decompositions. Equation 2 above shows a typical reaction of the hydrochloric acid group precipitation.

The hydrogen sulfide group is precipitated by reactions of the various metal salts with hydrogen sulfide, the group reagent. For example, in the case of copper nitrate, copper sulfide is formed.

$$Cu(NO_3)_2 + H_2S \rightarrow CuS\downarrow + 2\ HNO_3 \qquad (5)$$

Two different reactions occur in the precipitation of the ammonium sulfide group. Aluminum and chromium salts react with ammonium hydroxide to form aluminum and chromium hydroxides.

$$Al(NO_3)_3 + 3\ NH_4OH \rightarrow Al(OH)_3\downarrow + 3\ NH_4NO_3 \qquad (6)$$

Salts of the other metals do not react with ammonium hydroxide

to form precipitates, but react with ammonium sulfide giving sulfides.

$$Fe(NO_3)_2 + (NH_4)_2S \rightarrow FeS\downarrow + 2\ NH_4NO_3 \qquad (7)$$

In the ammonium carbonate group the various salts react with the group reagent, ammonium carbonate, to precipitate the slightly soluble barium, calcium and magnesium carbonates.

$$Ba(NO_3)_2 + (NH_4)_2CO_3 \rightarrow BaCO_3\downarrow + 2\ NH_4NO_3 \qquad (8)$$

Equations in the ionic form for these reactions are simpler and show more clearly what happens than Equations 5 to 8. Instead of Equations 5, 6, 7, and 8 the following can be written.

$$Cu^{++} + S^{--} \rightarrow CuS\downarrow \qquad (9)$$

$$Al^{+++} + 3\ OH^- \rightarrow Al(OH)_3\downarrow \qquad (10)$$

$$Fe^{++} + S^{--} \rightarrow FeS\downarrow \qquad (11)$$

$$Ba^{++} + CO_3^{--} \rightarrow BaCO_3\downarrow \qquad (12)$$

Equation 9 signifies that when a substance furnishing copper ion and a substance furnishing sulfide ion are brought together in solution, copper ion unites with sulfide ion to form copper sulfide, which is precipitated. The ions accompanying the copper and sulfide ions, respectively, may or may not react with each other. With them, however, we are not at present concerned. The other ions of the hydrogen sulfide group act like copper ion; each unites with sulfide ion to form a slightly soluble sulfide. The meaning of the other equations is similar.

QUESTIONS

1. Make from memory an outline showing the separation of all the groups in the scheme of analysis. Quantities and concentrations of the reagents may be omitted.

2. Make from memory an outline giving the steps that would be taken in showing that a certain solution contained the hydrochloric acid group and possibly also the alkali group, but none of the others.

3. Define the following terms: solution, saturated solution, precipitate, filtrate, decantation, group reagent, mother liquor, ion.

4. Write a molecular equation for the reaction of each of the following salts with the group reagent of the group to which the metal ion of the salt belongs:

$HgNO_3$	$Pb(NO_3)_2$	$Ni(NO_3)_2$
$Bi_2(SO_4)_3$	$FeCl_2$	$MnSO_4$
$CaCl_2$	$Cr(NO_3)_3$	$SnCl_2$
$SbCl_3$	$AsCl_3$	$PbCl_2$
$AlCl_3$	$HgCl_2$	$ZnSO_4$

5. Rewrite the equations of Question 4 in the ionic form.

6. Why do we wash precipitates after filtration? (Exercise 3, Section *d*.)

7. What ions will be present when each of the following substances are dissolved in water: hydrochloric acid, sulfuric acid, sodium hydroxide, ammonium hydroxide, silver nitrate, copper sulfate, sodium carbonate?

8. What ion is found in all acid solutions? What ion is found in all basic solutions? Could any salt beside copper sulfate supply copper ion when dissolved in water? Can a solution contain only one kind of ion?

9. What conditions must be met before an ion can be removed from a solution by filtration? (Section 6). Does precipitation ever *completely* remove a given kind of ion from solution? Is any precipitate ever absolutely insoluble?

CHAPTER III

THE ANALYSIS OF THE GROUP PRECIPITATES AND FURTHER EXERCISES

In this chapter general directions are given for all the further experimental work necessary as a preliminary to the actual analysis of unknown materials. The analysis of each of the group precipitates obtained in Exercise 3 is taken up in Exercises 4 to 8. Exercise 9 shows how some of the negative ions, such as chloride ion, nitrate ion, and sulfide ion, can be detected. Exercise 10 gives directions for the analysis of an unknown solid material. These exercises should be taken up in the order of their numbers till the whole series is finished. After that the Instructor may be consulted as to further laboratory work.

Each exercise gives only general directions and refers to the succeeding chapters for detailed directions. For example Exercise 4 is on the analysis of the hydrochloric acid group and refers to Chapter IV for detailed directions. The directions given in Chapters IV to VIII are written so that they can be used for the analysis of the metallic part of other unknown materials. Accordingly they include and repeat the directions given in Exercise 3 for making a separation of the groups. In using Chapters IV to VII in the analysis of the group precipitates obtained in Exercise 3 it is necessary to omit that part of each chapter which describes the precipitation of the group. Exercises 4 to 8 below give more specific instructions as to the analysis of the group precipitates of Exercise 3. These instructions should be carefully read and followed.

Following the experimental sections in each of Chapters IV to VIII is a section in which the reactions of the experimental part are discussed, and at the end of each chapter there are some questions. A study of the reactions and questions should be considered parts of Exercises 4 to 8 as well as the laboratory work. The object of the work should be not to follow mechanically the directions, but to gain familiarity with the chemical principles involved and with the substances used.

EXERCISE 4

Analysis of the Hydrochloric Acid Group Precipitate

If a hydrochloric acid group precipitate was obtained in Exercise 3 this precipitate should now be analyzed as directed in the next paragraph. In some cases, however, no precipitate will have been obtained for the hydrochloric acid group. If this was the case the next paragraph should be omitted, and a separate solution should be made up and analyzed as directed in the third paragraph of this exercise.

Transfer the hydrochloric acid group precipitate obtained in Exercise 3 to a newly prepared filter. A stirring rod may be of help in doing this. If it is desirable to wash some of the precipitate from the old filter or from the test tube in which it was kept, a 2 *M* hydrochloric acid solution like that with which the precipitate was washed in Exercise 3 should be used rather than water, and it should be used sparingly. When the precipitate is on the new filter, analyze it according to the directions in Section 18, page 31, "Analysis of the Group Precipitate." Omit Section 17 entitled "Precipitation of the Group."

If no hydrochloric acid group was obtained in Exercise 3, make up a solution containing lead, mercurous and silver ions by mixing 2 cc. of lead nitrate solution, 2 cc. of mercurous nitrate solution and 2 cc. of silver nitrate solution. Precipitate the hydrochloric acid group from this solution and analyze the precipitate according to the directions in Chapter IV, starting at the beginning, Section 17.

16. Notebook Record. The results of the laboratory work should be recorded in a notebook as soon as they are obtained. This record should be sufficiently complete and up to date so that if an unfinished experiment stands from one laboratory period to the next the record will show where to resume the work. It should be written in such a way that the Instructor can read it and understand it. It is desirable that the record be made in a permanent notebook at the time when the work is being done, but it is not expected that this record will be as neat and orderly as if it were written outside the laboratory. The following form is suggested as being simple and sufficient.

EXERCISE IV

ANALYSIS OF THE HCL GROUP FROM EXERCISE 3

Tested for	Result	Remarks	Report
Pb^{++}	+	Small amount	Pb
Hg^{+}	−	− − −	
Ag^{+}	+	Large precipitate	Ag

The title describes the material analyzed. The first column at the left tells what tests were made. The second column tells whether the results of the test were positive or negative. The third column is the place for remarks or notes of unusual behavior and need not be filled out in every case. In the last column are recorded all those ions which are considered to have been present in significant quantities in the original sample. Such a record should be made for Exercise 4 and for each of the following exercises.

It is to be noted that in the form suggested the thing tested for might be a whole group of ions instead of a single one. Thus the results of Exercise 3 might be recorded in the same way, the things tested for being the hydrochloric acid group, the hydrogen sulfide group, and so on, and a positive or negative test being recorded for the whole group in each case. Such entries will be useful in recording the results of the analysis of unknowns, when, as will often be the case, whole groups are found to be absent.

EXERCISE 5

Analysis of the Hydrogen Sulfide Group Precipitate

When the analysis of the hydrochloric acid group has been made and the results have been recorded, analyze the hydrogen sulfide group obtained in Exercise 3. Directions for this are to be found in Chapter V, page 35, starting with Section 24, entitled "Separation into Sub-groups," and continuing through Sections 25 and 26 to the end of the experimental part of the chapter. Section 23, "Precipitation of the Whole Group," must be omitted.

In the separation of the copper and tin sub-groups, Section 24, it may be found that the tin sub-group is entirely absent. If this is the case, make up a solution containing the ions of the tin group by mixing 2 cc. of arsenious chloride solution, 2 cc. of antimonous chloride solution and 2 cc. of stannous chloride solution. Analyze the solution according to the directions in Chapter V, starting at the beginning of the directions for the analysis of the hydrogen sulfide group, page 34, Section 23, "Precipitation of the Whole Group."

EXERCISE 6

Analysis of the Ammonium Sulfide Group Precipitate

When the analysis of the hydrogen sulfide group precipitate has been completed, analyze the ammonium sulfide group precipitate, following the directions in Section 40, page 55. Omit Section 39 entitled "Precipitation of the Group."

EXERCISE 7

Analysis of the Ammonium Carbonate Group Precipitate

When the analysis of the ammonium sulfide group precipitate has been completed, analyze the carbonate group precipitate, following the directions in Section 51, page 71. Omit Sections 49 and 50 entitled "Preparation of the Solution," and "Precipitation of the Ammonium Carbonate Group," respectively.

EXERCISE 8

Analysis of the Alkali Group

The alkali group is present in the filtrate from the ammonium carbonate group, the other groups having been precipitated and filtered off in Exercise 3. The alkali group is not precipitated as a group.

Test the solution containing the alkali group for sodium and potassium ions according to the directions in Sections 55, 56, and 57, starting on page 76. Omit the test for ammonium ion, as this test must be made on the original material.

EXERCISE 9

Tests for Negative Ions

(*a*) *Chloride, Nitrate and Sulfate Ions.* Prepare a solution containing chloride, nitrate and sulfate ions by mixing 2 cc. of mercuric chloride solution, 2 cc. of copper nitrate solution and 2 cc. of ferrous sulfate solution. Digest this with 25 cc. of 1.5 *M* sodium carbonate solution as described in Section 63*a* page 82 to precipitate the metallic ions, filter and test portions of the filtrate for chloride, nitrate and sulfate ions as described in Sections 63*b*, 63*c*, and 63*d*.

(*b*) *Carbonate and Sulfide Ions.* Put about 0.1 g. of sodium carbonate on a watch glass and test it for carbonate ion as described in Section 64, page 84. Then clean the watch glass and make the same test with 0.1 g. of ferrous sulfide.

EXERCISE 10

The Analysis of an Unknown Solid Material

Obtain an unknown solid material for analysis. This may be a mixture of salts, metals, or metallic oxides. The metallic ions or metals of this mixture may be detected by the procedures given in Chapters IV to VIII inclusive provided that the mixture first be gotten into solution. To accomplish this, prepare a sample as described in Section 69, page 89, and then try to dissolve it by the procedure given in Section 70. Subsequent treatment will depend somewhat on which reagent was used to dissolve the unknown. Section 70 includes directions as to how to proceed with the analysis.

In carrying out the analysis it is better to analyze each group precipitate as soon as it is filtered and washed rather than to set it

aside and precipitate the other groups first. A solution can be preserved more conveniently than a precipitate.[1]

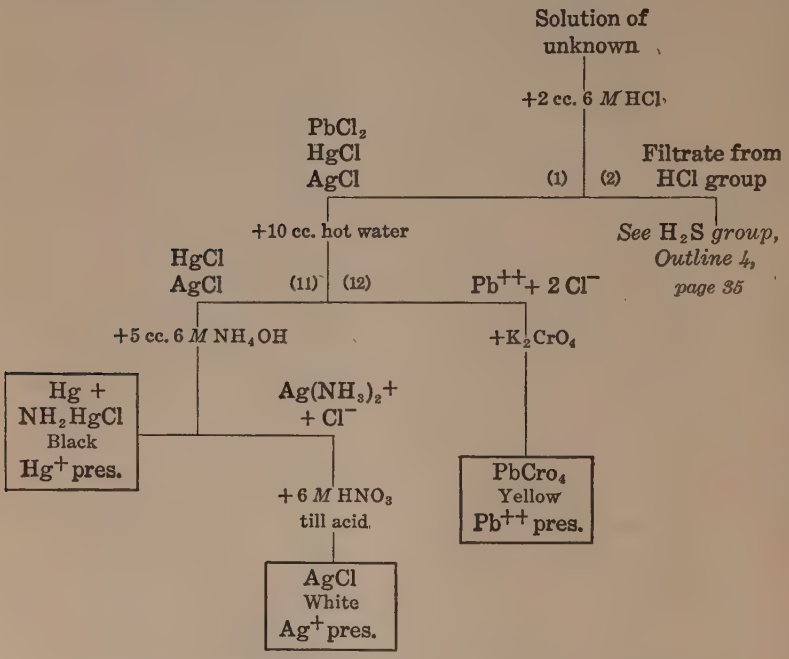
When the metallic ions have been detected, weigh out about 0.5 g. of the powdered solid (unless the unknown is a metal or alloy, in which case the analysis is already complete) and treat it by the procedures of Section 63, page 82, for the detection of chloride, nitrate and sulfate ions. Finally test for carbonate and sulfide ions as described in Section 64.

[1] In the analysis of the practice solution, Exercises 3 to 8, it was directed that the opposite order be followed because it was considered that that gave a better chance for comprehension of the scheme of analysis.

CHAPTER IV

THE HYDROCHLORIC ACID GROUP

The hydrochloric acid group consists of ions which unite with chloride ion to form slightly soluble chlorides, namely lead, silver, and mercurous ions. The group is precipitated by the addition of hydrochloric acid to a solution containing any or all of the metallic ions. Outline 3 shows the procedure for precipitating and analyzing the hydrochloric acid group, and Sections 17 and 18 give the procedure in detail.



OUTLINE 3. Precipitation and analysis of the hydrochloric acid group.

17. Precipitation of the Group. To the solution containing the positive ions of the unknown material add 2 cc. of 6 *M* hydrochloric acid to precipitate the group, and filter. Remove the

filtrate and reserve it for the precipitation of the other groups. Wash the precipitate with two 5 cc. portions of 2 *M* hydrochloric acid and throw away the wash solution.

18. Analysis of the Group Precipitate. Wash the precipitate on the filter with about 10 cc. of hot water, allowing the water to run through the filter into a test tube. Add to the filtrate in the test tube a few drops of potassium chromate solution to test for lead. A yellow precipitate of lead chromate indicates the presence of lead ion. Absence of a precipitate indicates the absence of lead ion, although it still may be found present in the hydrogen sulfide group.

A residue remaining on the paper may be mercurous chloride or silver chloride or undissolved lead chloride or any combination of these. Pour over the residue 5 cc. of 6 *M* ammonium hydroxide and catch the filtrate in a test tube. Blackening of the residue on the filter indicates the presence of mercurous ion.

Acidify the filtrate with nitric acid; this will require 5 cc. or more of the 6 *M* acid. A white precipitate indicates the presence of silver ion.

Reactions of the Hydrochloric Acid Group

19. Precipitation. The precipitation of the hydrochloric acid group is the result of the union of the lead, silver and mercurous ions with chloride ion to form slightly soluble precipitates of lead chloride, silver chloride and mercurous chloride, respectively.

The precipitate is washed with 2 *M* hydrochloric acid rather than with water because solid chlorides are less soluble in solutions containing a moderate amount of chloride ion than they are in pure water.

20. Lead. When the group precipitate is washed with the 10 cc. of hot water, the lead chloride, if present, is usually dissolved in sufficient quantity to permit the confirmatory test to be made. Hot water is used because the solubility of lead chloride is much greater in hot water than in cold water. However, pouring the hot water over the precipitate once will not dissolve all the lead chloride present in the precipitate unless the quantity is quite small. Undissolved lead chloride in the group precipitate seldom interferes with the later tests for mercury and silver. Lead chromate is less soluble than lead chloride and the addition of chromate ion to a solution of lead chloride gives a precipitate of lead chromate.

21. Silver. In connection with the reaction by which silver chloride is dissolved when 5 cc. of 6 *M* ammonium hydroxide is poured over the mixture of mercurous and silver chlorides, it should be recalled that an ammonium hydroxide solution contains ammonia molecules (NH_3), as well as ammonium ions (NH_4^+), and hydroxide ions (OH^-), and that each of these is capable of reacting independently with other ions or molecules. Silver chloride reacts with the dissolved ammonia molecules to form a soluble compound.

$$AgCl + 2\ NH_3 \rightarrow AgCl \cdot 2\ NH_3 \qquad (13)$$

The dot in the formula of the product indicates that the valence relations existing in the molecule are little understood. A similar implication follows when we write $CuSO_4 \cdot 5\ H_2O$. The formula $AgCl \cdot 2\ NH_3$ is more frequently written $Ag(NH_3)_2Cl$. Both formulas represent the same substance, which is called silver-ammonia chloride. It may be obtained in the solid state. When solid silver-ammonia chloride is dissolved in water it ionizes to give silver-ammonia ion and chloride ion.

$$Ag(NH_3)_2Cl \rightarrow Ag(NH_3)_2^+ + Cl^- \qquad (14)$$

The action of ammonia on a solid silver chloride precipitate can be represented by a single equation which combines equations 13 and 14.

$$AgCl + 2\ NH_3 \rightleftarrows Ag(NH_3)_2^+ + Cl^- \qquad (15)$$

The silver-ammonia ion is composed of one silver ion and two molecules of ammonia. Ions of this kind are called complex ions and are frequently met in qualitative analysis. The silver-ammonia ion does not react with chloride ion to form a precipitate, but when sufficient nitric acid is added to a solution containing silver-ammonia ion and chloride ion the silver-ammonia ion is broken up and a precipitate of silver chloride results.

$$Ag(NH_3)_2Cl + 2\ HNO_3 \rightarrow AgCl\downarrow + 2\ NH_4NO_3 \qquad (16)$$

The same reaction can be represented by two ionic equations.

$$Ag(NH_3)_2^+ + 2H^+ \rightarrow Ag^+ + 2\ NH_4^+ \qquad (17)$$

$$Ag^+ + Cl^- \rightarrow AgCl\downarrow \qquad (18)$$

The significant point is that on account of the formation of the complex silver-ammonia ion, silver ion is removed from the solution to such an extent that the solution no longer responds to tests for silver ion so long as the solution is basic. When the silver-ammonia ion is decomposed by the addition of hydrogen ion, silver ion is again present in sufficient quantity to permit the tests.

22. Mercury. The black residue obtained when ammonium hydroxide solution is poured over the mercurous chloride precipitate is a mixture of finely divided metallic mercury and the white compound NH_2HgCl. Most metals when finely divided appear to be black in color. The compound NH_2HgCl is formed by an oxidation-reduction reaction.

QUESTIONS

1. Make from memory an outline showing the separation and detection of all the ions in the hydrochloric acid group, starting with the precipitation of the group. Quantities and concentrations of reagents may be omitted.

2. Make outlines showing the steps necessary for the analysis of the hydrochloric acid group (a) if only lead ion was present, (b) if only mercurous ion was present.

3. Could a solution of copper chloride be used to precipitate the hydrochloric acid group? Is there any objection to its use?

4. Why is 2 *M* hydrochloric acid used rather than water to wash the hydrochloric acid group precipitate?

5. Can lead chloride be more completely precipitated from a hot or from a cold solution? Why?

6. Write molecular and ionic equations showing the use of potassium chromate to confirm the presence of lead ion. Could sodium or ammonium chromate probably be used in place of potassium chromate?

7. Write molecular and ionic equations illustrating the dissolving of silver chloride by ammonium hydroxide.

8. Write molecular and ionic equations illustrating the precipitation of silver chloride by nitric acid in the final confirmatory test for silver.

9. Explain why complex silver-ammonia ion could not be formed in a solution that was acid to litmus.

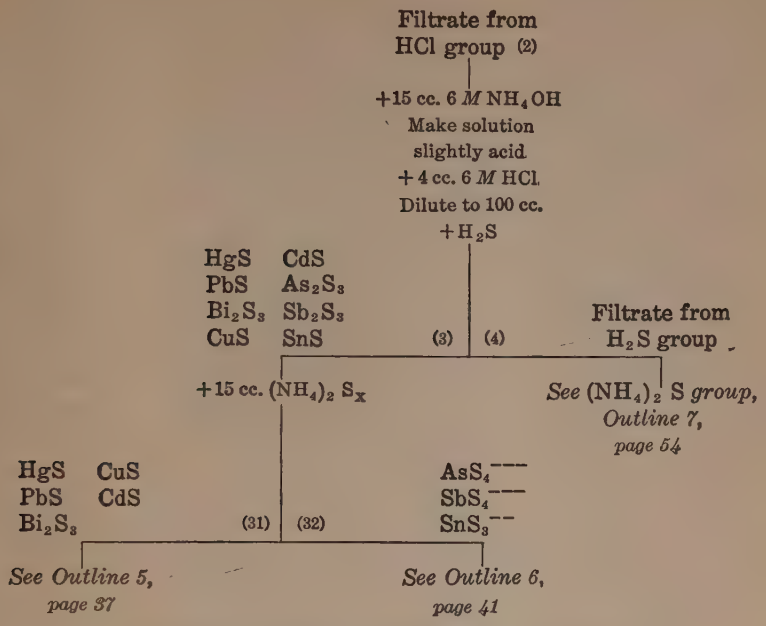
10. What ions and molecules exist in an ammonium hydroxide solution?

CHAPTER V

THE HYDROGEN SULFIDE GROUP

The hydrogen sulfide group consists of those ions, with the exception of silver and mercurous ions, which can unite with the sulfide ion of hydrogen sulfide in an acid solution to form sulfide precipitates. It is precipitated by first carefully regulating the acid concentration, or more properly the hydrogen ion concentration, of the solution, and then saturating the solution with hydrogen sulfide gas. The group is divided into two sub-groups. By treatment of the precipitated sulfides with ammonium polysulfide, the sulfides of arsenic, antimony and tin are dissolved and can be separated from the others by filtration. These are the tin group. The others constitute the copper group. Outline 4 shows the precipitation of the group and the separation of the copper and tin groups, and Outlines 5 and 6, respectively, show the analyses to these sub-groups. The procedure is given in detail in Sections 23 to 26.

23. Precipitation of the Whole Group. The hydrogen sulfide group is to be precipitated from the filtrate from the hydrochloric acid group. To the filtrate from the hydrochloric acid group add 15 cc. of 6 *M* ammonium hydroxide and shake well. If the solution is not basic to litmus, continue the addition of 1 cc. portions of 6 *M* ammonium hydroxide till the solution, after shaking, is basic to litmus. The addition of ammonium hydroxide may cause a precipitate to form but this will not interfere. Then add 6 *M* hydrochloric acid 1 cc. at a time till the solution is acid to litmus. Finally add just 4 cc. of 6 *M* hydrochloric acid in excess. If there should be a colored precipitate left after the addition of the acid, heat till it dissolves. A white precipitate will do no harm. Dilute the solution to 100 cc. with distilled water, disregarding any precipitate that is formed, and put it into the precipitation flask. Pass in hydrogen sulfide gas, shaking the flask continuously, till the solution is saturated with the gas. Then boil the solution containing the precipitate for one minute. Filter and save the filtrate. Wash the precipitate



OUTLINE 4. Precipitation of the hydrogen sulfide group and separation into subgroups.

with a hydrogen sulfide solution as in Exercise 3, page 14. The wash solution can be thrown away.

Before proceeding, the filtrate should be tested to see if precipitation was complete. Heat the filtrate to the boiling point and pass in more hydrogen sulfide. Allow the solution to cool considerably before disconnecting the flask from the source of hydrogen sulfide. Absence of a colored precipitate shows that precipitation was complete the first time. In this case the solution can be set away till the ammonium sulfide group is to be precipitated.

If there is a precipitate on second addition of hydrogen sulfide the mixture must be filtered and the precipitate must be washed and united with the first one for the treatment below. After filtering off the second precipitate, the filtrate must be tested again for completeness of precipitation, and treatment must be repeated till precipitation is complete.

24. Separation into Sub-groups. Transfer the hydrogen sulfide group precipitate to a casserole without the addition of

water and add 15 cc. of 3 *M* ammonium polysulfide, $(NH_4)_2S_x$. These two operations can be conveniently done at one time by making a hole in the filter paper and washing the precipitate through by pouring the 15 cc. of solution repeatedly over the precipitate, loosening the precipitate if necessary by means of a glass rod. Another method is to put paper and precipitate into the casserole, add the 15 cc. of solution, agitate the mixture and scrape the paper with a glass rod to remove the precipitate and finally take out the paper. If the precipitate has been preserved in a test tube under water, perhaps nearly all of the water can be poured off. Then the precipitate can be washed into the casserole with the ammonium polysulfide solution. If the water can not be poured off from the precipitate it should be filtered off. The precipitate can then be transferred to the casserole as described above.

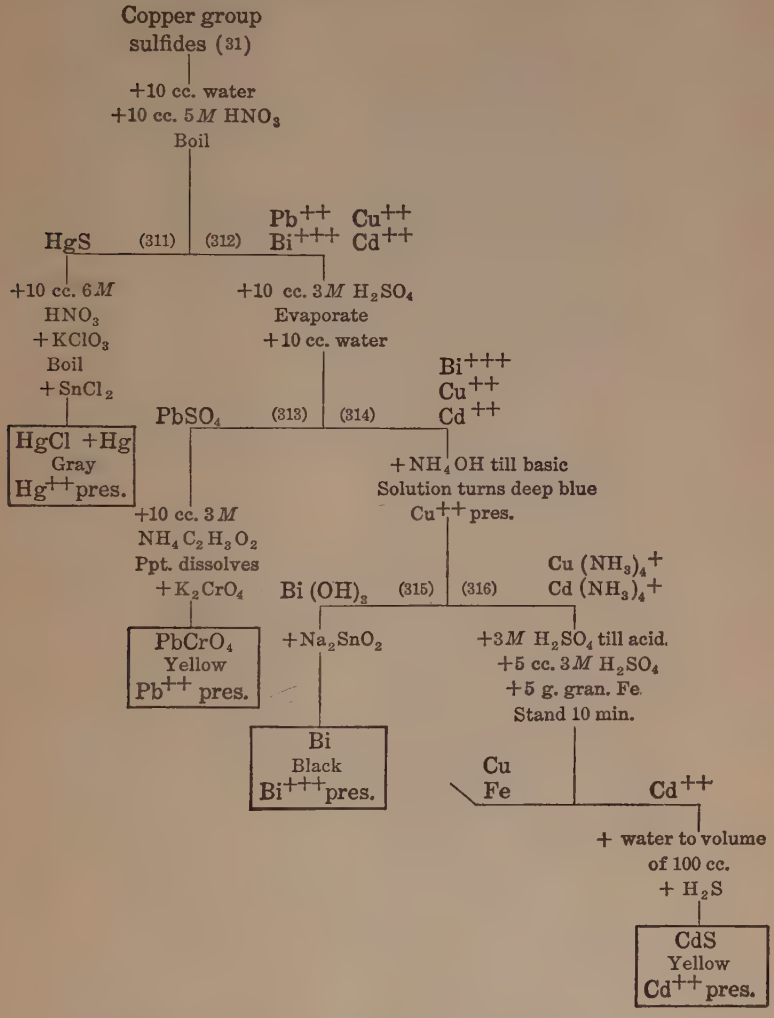
After mixing the precipitate and the ammonium polysulfide solution in the casserole, heat to about 60° C., *but do not boil.* Arsenic, antimony and tin sulfides react to form the ions AsS_4^{---}, SbS_4^{---}, and SnS_3^{--} which pass into the solution. The other sulfides are not affected. Filter, and wash the precipitate which remains on the filter twice with water, rejecting the washings.

Test the filtrate containing the ammonium polysulfide to see whether or not the tin group is present by adding 12 cc. of 6 *M* hydrochloric acid, then more, 1 cc. at a time till the solution is acid to litmus. A nearly white, finely divided precipitate is sulfur. A precipitate of nothing but sulfur indicates that the tin group is absent. In this case omit the analysis of the tin group, Section 26, and analyse the copper group precipitate as directed in Section 25 below.

If a yellow, brown or orange precipitate is formed when the filtrate obtained in the ammonium polysulfide treatment is acidified, the tin group is present. If there is no precipitate left on the filter, the separation is complete and the copper group is absent. The tin group precipitate can then be analyzed as directed in Section 26.

If the tin group is present and a precipitate remains on the filter, the precipitate must be tested to see if the separation has been complete. Treat the precipitate with 5 cc. of ammonium polysulfide solution, heating to about 60° C., and filter. Acidify

the filtrate to see if any more of the tin group is present in it. If a precipitate of nothing but sulfur is obtained, the separation was complete the first time. Reject both solution and sulfur


Copper group sulfides (31)
+10 cc. water
+10 cc. 5M HNO3
Boil
HgS (311) (312) Pb++ Bi+++ Cu++ Cd++
+10 cc. 6M HNO3 +KClO3 Boil +SnCl2
+10 cc. 3M H2SO4 Evaporate +10 cc. water
HgCl +Hg Gray Hg++ pres.
PbSO4 (313) (314) Bi+++ Cu++ Cd++
+NH4OH till basic Solution turns deep blue Cu++ pres.
+10 cc. 3M NH4C2H3O2 Ppt. dissolves +K2CrO4
Bi(OH)3 (315) (316) Cu(NH3)4+ Cd(NH3)4+
PbCrO4 Yellow Pb++ pres.
+Na2SnO2
+3M H2SO4 till acid. +5 cc. 3M H2SO4 +5 g. gran. Fe Stand 10 min.
Bi Black Bi+++ pres.
Cu Fe
Cd++
+ water to volume of 100 cc. + H2S
CdS Yellow Cd++ pres.

OUTLINE 5. Analysis of the copper group.

precipitate. A precipitate remaining on the filter then means that the copper group is present.

If a yellow, brown or orange precipitate is obtained on acidify-

ing the second ammonium polysulfide filtrate, add the precipitate to the similar one obtained in the first treatment with ammonium polysulfide. Treat the precipitate on the filter, presumably the copper group, with another 5 cc. portion of ammonium polysulfide solution. Continue the treatments till the ammonium polysulfide filtrate after treatment gives a precipitate of nothing but sulfur on acidifying. Combine all the various mixtures containing portions of the tin group and set the mixture aside till the tin group is to be analyzed.

If both copper and tin groups are present, analyze the copper group first as directed in Section 25 and save the tin group, without filtering, till it can be analyzed as directed in Section 26.

25. Analysis of the Copper Group. (*a*) *Mercury.* Wash the copper group precipitate into a casserole by means of a stream of water from the wash bottle. If the volume of water in the casserole is more than 10 cc., allow the precipitate to settle and pour off the excess. If it is much less than 10 cc., add a little water. Add 10 cc. of 6 *M* nitric acid and boil the mixture about half a minute. Filter and save the filtrate, which may contain all the ions of the copper group except mercuric ion. If the residue is black, wash it, throwing away the wash solution. Treat the residue as described in the next paragraph. If the residue is light colored, absence of mercuric ion is indicated but not proved, and the next paragraph should not be omitted.

Put the residue with the filter paper into a casserole and pour over it 10 cc. of 6 *M* hydrochloric acid. Rinse the residue from the filter paper. Remove the filter paper and throw it away. Heat the solution to boiling. If the black residue does not dissolve or become nearly white in color, add solid potassium chlorate in very small portions, stirring after each addition, till the residue dissolves or becomes nearly white in color. Boil for a minute to expel the excess chlorine. Dilute with about 10 cc. of water and if necessary filter out the sulfur residue, which can be thrown away. Test for mercuric ion by adding stannous chloride solution, first a drop or two, and then about 2 cc. A white precipitate, which turns gray as more stannous chloride is added, shows the presence of mercuric ion.

(*b*) *Lead.* To the solution containing the other four ions of the copper group add 10 cc. of 3 *M* sulfuric acid. Put the solution into a casserole and evaporate (with the dish near a hole in

the fume duct or under a hood) till white fumes of sulfur trioxide appear. These fumes do not disappear as soon after they leave the dish as the steam and nitric acid vapors which come off first. Cool the mixture and pour it, a little at a time, into 10 cc. of cold water in a test tube. Rinse out the casserole with a little of the solution and pour the rinsings into the test tube. Let the mixture stand for about 5 minutes. Absence of a precipitate shows the absence of lead ion. In this case the solution need not be filtered, but can be treated as described below for the detection of bismuth, copper and cadmium ions. If there is a precipitate it is probably lead sulfate. Filter it out. Save the filtrate to test for bismuth, copper and cadmium ions. If lead ion was found in the hydrochloric acid group, it is unnecessary to test the precipitate; it can be thrown away, and the next paragraph can be omitted. If lead ion was not found in the hydrochloric acid group the precipitate must be tested as described in the next paragraph.

Wash the lead sulfate precipitate with a little water, throwing away the washings, then pour on it 10 cc. of ammonium acetate solution, catching the solution in a test tube as it runs through the filter. Add to the filtrate a few drops of potassium chromate solution. A yellow precipitate shows the presence of lead ion.

(*c*) *Bismuth and Copper.* To the solution which may contain bismuth, copper and cadmium ions add 15 cc. of 6 *M* ammonium hydroxide and mix well, and if necessary add more, 5 cc. at a time, till the solution is distinctly basic, or turns to a darker blue color than it was originally. If the solution turns to a darker blue color when it becomes basic, the presence of copper ion is shown. Absence of this color change shows the absence of copper ion. Absence of precipitate shows the absence of bismuth ion. In the latter case filtration is unnecessary and the solution, as it is, can be treated for the detection of cadmium ion as directed below. If a precipitate is formed, it is probably bismuth hydroxide. Filter it off, saving the filtrate for the detection of cadmium ion.

Wash the precipitate twice with water, throwing away the washings. Prepare a solution of sodium stannite by taking 1 cc. of stannous chloride ($SnCl_2$) solution (do not use stannic chloride, $SnCl_4$) and adding sodium hydroxide solution (do not use ammonium hydroxide) and mixing till the solution is clear after

shaking and addition of more sodium hydroxide does not cause a precipitate to form. Pour some of the sodium stannite solution on the bismuth hydroxide precipitate. If the precipitate turns black, owing to the formation of free bismuth in a finely divided state, the presence of bismuth ion is confirmed.

(*d*) *Cadmium.* If copper ion is present in the filtrate from the bismuth hydroxide it must be removed by the procedure given below before this solution is tested for cadmium ion. If copper ion is absent, the part of the procedure calling for the addition of powdered iron, allowing the solution to stand and filtering can be omitted.

To the filtrate from the bismuth hydroxide (or to the solution which was tested for bismuth ion if the latter was found absent) add 3 *M* sulfuric acid 1 cc. at a time till the solution is acid, then add 5 cc. in excess. The solution should then have a volume of 30 to 50 cc. Add 5 g. of granulated iron and mix with the solution. Allow the mixture to stand for ten minutes, shaking and stirring it occasionally. Filter off the excess iron and precipitated copper and reject them. To the filtrate, which may contain the cadmium ion, add 2 cc. of 3 *M* sulfuric acid and enough water to make the total volume 100 cc. Pass in hydrogen sulfide gas. A yellow precipitate of cadmium sulfide shows the presence of cadmium ion.

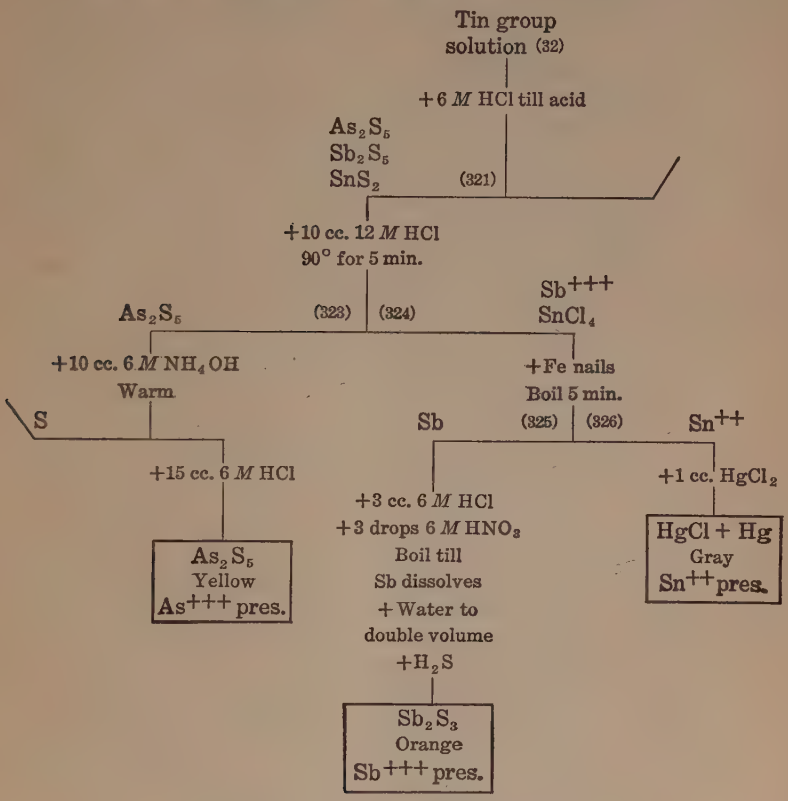
If the precipitate is dark colored, making it doubtful whether or not cadmium ion is present, filter and dissolve the precipitate by pouring 3 *M* sulfuric acid over the filter and catching the filtrate. To this filtrate add 6 *M* ammonium hydroxide till the solution is basic, filter out any precipitate formed, and treat the filtrate as described above for the separation of copper and cadmium ions.

26. The Tin Group. Filter the tin group sulfides from the solution from which they were precipitated when the filtrate obtained in the separation of the copper and tin groups was acidified. Reject the filtrate. Analyze the precipitate according to the following directions.

(*a*) *Arsenic.* The arsenic may be separated from the antimony and tin as follows. Transfer the precipitate to a test tube and add 10 cc. of 12 *M* hydrochloric acid. Heat the test tube in a beaker of gently boiling water [1] for 5 to 10 minutes, continuing

[1] The beaker need not be more than half full of water. The less there is the quicker it will boil.

the treatment as long as action is apparent. Every minute or two during the treatment remove the test tube and shake the contents. Next filter, receiving the filtrate in a test tube. As the filtrate cools a precipitate may appear in it. This precipitate



OUTLINE 6. Analysis of the tin group.

belongs with the filtrate and the mixture should not be filtered again. Wash the precipitate with 6 *M* hydrochloric acid, throwing away the wash solution. The residue contains the arsenic while the filtrate contains the antimony and tin.

If an appreciable residue remains on the filter, test it for arsenic by transferring the filter paper and precipitate to a casserole containing 10 cc. of 6 *M* ammonium hydroxide. Warm (but do not boil) with frequent agitation. Then filter and add 15 cc. of 6 *M* hydrochloric acid to the filtrate. A yellow precipitate indicates the presence of arsenic.

(*b*) *Antimony.* To separate antimony from tin add two small iron nails [1] to the filtrate containing the antimony and tin ions. Keep the solution at or near the boiling point for 5 minutes. A dark colored precipitate indicates the presence of antimony. Absence of an appreciable precipitate shows absence of antimony. A few black specks may come from the nails. If a loose crust adheres to the nails, wash it into the filter with a stream of water. Save the filtrate for the test for tin ion. To confirm the presence of antimony in the precipitate on the filter, perforate the filter and wash the precipitate into a test tube by a small amount of water from the wash bottle. Add 3 cc. of 6 *M* hydrochloric acid, heat to boiling, then add a few drops of 6 *M* nitric acid and boil. This will dissolve the precipitate. Finally, place this solution in the precipitation flask, add an equal volume of water, and saturate the solution with hydrogen sulfide. An orange-colored precipitate confirms the presence of antimony.

(*c*) *Tin.* To the filtrate from the nail treatment add about 1 cc. of mercuric chloride solution. The formation of a gray or white precipitate indicates the presence of tin.

Reactions of the Hydrogen Sulfide Group

27. Precipitation. The precipitation of the hydrogen sulfide group results from the union of the various metal ions with the sulfide ion to form solid sulfides. Equation 5, page 5, is a typical equation. The source of the sulfide ion is the hydrogen sulfide. Hydrogen sulfide, besides being a very weak acid, that is, little ionized, is not very soluble in water, so that at best the concentration of the sulfide ion is small. The presence of hydrochloric acid, or any other strong acid, in the solution makes it still smaller. The reason why the addition of strong acids decreases the concentration of sulfide ion in a solution can be seen by considering the equation for the ionization of hydrogen sulfide.

$$H_2S \rightleftharpoons 2H^+ + S^= \qquad (19)$$

Since the reaction is reversible it will come to equilibrium. If the concentration of hydrogen ion in the solution is increased by the addition of a strong acid, the reaction will proceed from right

[1] If the surface of the nails is bright, the action may be slow in starting. This condition can be corrected by heating the nails in a test tube containing about 10 cc. of 6 *M* hydrochloric acid to which has been added 1 cc. of copper nitrate solution. As soon as hydrogen is evolved rapidly the nails are ready for use in the antimony separation. After use it is well to keep the nails for further use.

to left, in the reverse direction, using up hydrogen and sulfide ions, till a new equilibrium is reached in which the concentration of the sulfide ions will be less than in the first equilibrium.

To precipitate a metal sulfide the concentration of the sulfide ion in the solution must be larger than a definite minimum value. Why this is true will be explained in Chapter XII. This minimum has a different value for each different metal ion. If the concentration of hydrochloric acid in a solution is much larger than 0.3 *M* the sulfide ion concentration will become too small to precipitate some of the ions of the hydrogen sulfide group. Hence, it is important to see that the acid concentration is not greater than that called for in the directions. On the other hand if the acid concentration is much below 0.2 *M* the sulfide ion concentration may be great enough to precipitate some of the sulfides of the ammonium sulfide group along with the hydrogen sulfide group. The matter of correct adjustment of the hydrogen ion concentration of the solution in which the hydrogen sulfide precipitation is carried out is a matter of prime importance.

Sometimes a precipitate of nothing but sulfur is obtained when hydrogen sulfide is added to the filtrate from the hydrochloric acid group. In this case, of course, the hydrogen sulfide group is absent. The precipitate can be recognized as being merely sulfur by its color, which is nearly white, and by the fact that it is very finely divided and will not settle out leaving a clear solution. It will usually pass through a filter. The sulfides of the hydrogen sulfide group are either black or colored. Sulfur may be precipitated along with the sulfides also, but in this case its presence would not be noticed.

The precipitation of sulfur is caused by reaction of the sulfide ion with some substance which can act as an oxidizing agent. Ferric ion, Fe^{+++}, is such a substance. When ferric ion and sulfide ion are brought into the same solution, they react giving ferrous ion and sulfur.

$$2\ Fe^{+++} + S^{--} \rightarrow 2\ Fe^{++} + S\downarrow \qquad (20)$$

The ferric ion removes the negative charges from the sulfide ion, thus converting it into free sulfur, and is itself changed to ferrous ion by having one of its positive charges neutralized by a negative charge. In other words the ferric ion is reduced, while the sulfide ion is oxidized.

Nitric acid, if it is sufficiently concentrated, dichromate ion, $Cr_2O_7^{--}$, and permanganate ion, MnO_4^-, are other examples of oxidizing agents which can oxidize sulfide ion. If a precipitate of sulfur is observed when hydrogen sulfide is passed into the filtrate from the hydrochloric acid group, this fact should be carefully noted. It is an indication of the presence of an oxidizing agent. This information may be evidence as to the state of oxidation in the original solution of certain of the elements present.

It is useful to have the colors of the various sulfides in mind in order that full advantage may be taken of the appearance of precipitates. The sulfides of the copper group metals are all dark in color except cadmium sulfide, which is yellow. Mercuric, lead, and copper sulfides are black, while bismuth sulfide is dark brown. Arsenious and arsenic sulfides and stannic sulfide are yellow. Stannous sulfide is brown. Both of the antimony sulfides are orange to red.

28. Separation into Sub-groups. The dissolving of the tin group sulfides by an ammonium polysulfide solution involves some relatively unusual reactions. These are analogous to a more familiar reaction. If arsenic pentoxide, As_2O_5, is added to water, the two unite to form arsenic acid.

$$As_2O_5 + 3\ H_2O \rightarrow 2\ H_3AsO_4 \qquad (21)$$

This is an example of a general method of preparing acids. Oxygen is in the same group of the periodic classification of the elements as sulfur, and sulfides are sometimes analogous to oxides. It might be expected that arsenic sulfide and hydrogen sulfide would react in a similar manner.

$$As_2S_5 + 3\ H_2S \leftrightharpoons H_3AsS_4 \qquad (22)$$

This reaction, however, is reversible, as indicated by the double arrow, and the equilibrium lies far to the side of the arsenic sulfide and hydrogen sulfide. With ammonium sulfide in place of hydrogen sulfide, however, the reaction goes practically to completion toward the right.

$$As_2S_5 + 3(NH_4)_2S \rightarrow 2(NH_4)_3AsS_4 \qquad (23)$$

The compound formed is ammonium thioarsenate, the prefix "thio" indicating that the oxygen of the ordinary arsenate

radical has been replaced by sulfur. Ammonium thioarsenate is a soluble compound, so the result is that arsenic sulfide is dissolved by ammonium sulfide. Antimonic sulfide is quite like arsenic sulfide. The reaction of stannic sulfide with ammonium sulfide is similar.

$$SnS_2 + (NH_4)_2S \rightarrow (NH_4)_2SnS_3 \qquad (24)$$

If the tin group sulfides are in the lower state of oxidation they must be oxidized before they can be dissolved by ammonium sulfide. That is the reason why ammonium polysulfide is used for dissolving the tin group sulfides rather than ammonium sulfide. Ammonium polysulfide is made by adding sulfur to ammonium sulfide solution. The sulfur unites with some of the ammonium sulfide to form compounds of the nature of $(NH_4)_2S_2$. The prefix "poly" indicates that the average amount of sulfur per molecule is more than one atom and is somewhat indefinite. The formula is sometimes written $(NH_4)_2S_x$. It can be considered that ammonium polysulfide oxidizes the sulfides of the tin group metals by giving sulfur to them.

$$As_2S_3 + 2(NH_4)_2S_2 \rightarrow As_2S_5 + 2(NH_4)_2S \qquad (25)$$

$$SnS + (NH_4)_2S_2 \rightarrow SnS_2 + (NH_4)_2S \qquad (26)$$

Equation 25 can be combined with Equation 23 to give an equation for the whole reaction of ammonium polysulfide with arsenious sulfide.

$$As_2S_3 + 2(NH_4)_2S_2 + (NH_4)_2S \rightarrow 2(NH_4)_3AsS_4 \qquad (27)$$

Similarly Equation 26 can be combined with Equation 24. Equation 27 could also be written in the ionic form

$$As_2S_3 + 2\ S_2^{--} + S^{--} \rightarrow 2\ AsS_4^{---} \qquad (28)$$

The copper group sulfides are so little affected by the ammonium polysulfide reagent that a satisfactory separation can be made by treating the precipitate of the whole group with ammonium polysulfide and filtering. Copper sulfide, however, is dissolved to a small extent by the ammonium polysulfide solution. For this reason sodium sulfide is sometimes used instead of ammonium sulfide. The former has no appreciable effect on copper sulfide, but dissolves mercuric sulfide, so that with this procedure mercuric ion becomes one of the tin group.

29. The Copper Group. Lead, bismuth, copper and cadmium sulfides are dissolved by nitric acid, giving the corresponding nitrates. The reactions which take place are oxidation-reduction reactions. This is shown by the products; nitric oxide is given off and sulphur is formed. Writing equations for such reactions is often a more complicated procedure than writing equations for double decomposition reactions. Some of the theory of oxidation-reduction reactions and a method of working out equations for the more difficult ones are given in Chapter XIV. The reactions of the sulfides of the copper group with nitric acid are fairly complicated, as illustrated by the equation for the case of copper sulfide.

$$3\ CuS + 8\ HNO_3 \rightarrow 3\ Cu(NO_3)_2 + 4\ H_2O + 2\ NO + 3\ S\downarrow \quad (29)$$

Here the copper sulfide is oxidized and the nitric acid is reduced. The equations for the reaction of the other sulfides with nitric acid are quite similar to this one.

30. Mercury. Mercuric sulfide is not dissolved by dilute nitric acid, but is converted to the soluble mercuric chloride by an acid solution containing chlorine.

$$HgS + Cl_2 \rightarrow HgCl_2 + S\downarrow \quad 30)$$

The dissolving of a precipitate is the reverse of its precipitation. All precipitates dissolve to some extent, but when the ion concentrations in the solution reach the point at which precipitation would begin in the reverse process, the dissolving stops. To make a precipitate continue to dissolve it is necessary that at least one of the ions be either removed or destroyed as fast as it comes into solution. In the case of mercuric sulfide, the sulfide ion is destroyed by being oxidized to sulfur by the chlorine.

$$S^{--} + Cl_2 \rightarrow 2\ Cl^- + S\downarrow \quad (31)$$

In addition, the mercuric ion is removed by uniting with chloride ion to form mercuric chloride, which, differing from most salts, is ionized to only a small extent.

$$Hg + 2\ Cl^- \rightarrow HgCl_2 \quad (32)$$

The chlorine for the oxidation of the sulfide ion is supplied by the reaction of potassium chlorate and hydrochloric acid.

$$KClO_3 + 6\ HCl \rightarrow KCl + 3\ H_2O + 3\ Cl_2 \quad (33)$$

Hydrochloric acid is oxidized and potassium chlorate is reduced.

When stannous chloride is added to a solution containing mercuric chloride, the stannous chloride is oxidized to stannic chloride and the mercuric chloride is reduced to mercurous chloride which forms a white precipitate.

$$2\ HgCl_2 + SnCl_2 \rightarrow 2\ HgCl\downarrow + SnCl_4 \quad (34)$$

If more than enough stannous chloride for the reaction expressed by Equation 34 is added, the excess reacts with the mercurous chloride to give mercury.

$$2\ HgCl + SnCl_2 \rightarrow 2\ Hg\downarrow + SnCl_4 \quad (35)$$

In the finely divided state in which it is formed, the mercury is black. A combination of the white mercurous chloride and the black mercury gives a gray precipitate.

31. Lead. The reactions by which lead is separated and detected are double decompositions. The reaction taking place when the lead sulfate is dissolved by ammonium acetate solution deserves special notice.

$$PbSO_4 + 2\ NH_4C_2H_3O_2 \rightarrow (NH_4)_2SO_4 + Pb(C_2H_3O_2)_2 \quad (36)$$

When a slightly soluble substance can be formed by a double decomposition reaction, the reaction usually goes in such a way as to form it. Thus, it might be expected that Reaction 36 would go only from right to left rather than as shown, because lead sulfate is slightly soluble. The reaction goes as shown, however, because lead acetate is only slightly ionized. Lead sulfate is soluble to a slight extent, giving lead ions and sulfate ions in solution, and so the real reaction which takes place is

$$Pb^{++} + 2\ C_2H_3O_2^- \rightarrow Pb(C_2H_3O_2)_2 \quad (37)$$

As the lead ion is removed from the field of action, as indicated in Equation 37, more lead sulfate dissolves, till finally all of it is dissolved.

32. Bismuth. The precipitation of bismuth hydroxide is the result of a double decomposition. The test for bismuth, however, involves oxidation and reduction, the bismuth hydroxide being reduced to the black finely divided metallic bismuth by the stannite ion, which is oxidized to stannate ion.

$$2\ Bi(OH)_3 + 3\ SnO_2^{--} \rightarrow 2\ Bi\downarrow + 3\ SnO_3^{--} + 3\ H_2O \quad (38)$$

33. Amphoteric Hydroxides. The preparation of the sodium stannite brings to notice a class of compounds called amphoteric hydroxides, of which stannous hydroxide is an example. When a small amount of sodium hydroxide is added to stannous chloride solution, stannous hydroxide is precipitated, as would be expected.

$$SnCl_2 + 2\ NaOH \rightarrow Sn(OH)_2\downarrow + 2\ NaCl \qquad (39)$$

Stannous hydroxide appears to be a base here, and it would act like one. It can also act as an acid. When more sodium hydroxide is added, and the solution becomes basic, the stannous hydroxide acts as an acid (indicated by writing its formula H_2SnO_2) and is dissolved.

$$H_2SnO_2 + 2\ NaOH \rightarrow Na_2SnO_2 + 2\ H_2O \qquad (40)$$

A hydroxide which can act either as an acid or as a base is called an *amphoteric* hydroxide.

34. Copper and Cadmium. Complex Ions. The Electromotive Series. The action of copper and cadmium ions when ammonium hydroxide is added is similar to the action of silver ion under the same conditions. Copper and cadmium ions unite with ammonia to form complex ions.

$$Cu^{++} + 4\ NH_3 \rightarrow Cu(NH_3)_4{}^{++} \qquad (41)$$

$$Cd^{++} + 4\ NH_3 \rightarrow Cd(NH_3)_4{}^{++} \qquad (42)$$

In each case the complex ion differs considerably in properties from the parent ion from which it was formed. For example, while copper ion unites with hydroxide ion to form a precipitate, the complex ion does not. It is to be noticed that the number of ammonia molecules held by each of these metallic ions, as well as by silver ion, is twice the number of unit charges on the metallic ion.

The formation of the copper and cadmium complex ions prevents the precipitation of the hydroxides of copper and cadmium along with the bismuth hydroxide. The complex copper ion is the cause of the deep blue color in the solution, ordinary copper ion being a much lighter blue. When acid is added to the solution containing the complex ions, the ammonia leaves the complex ion to unite with hydrogen ion, forming ammonium ion.

$$Cu(NH_3)_4^{++} + 4\ H^+ \rightarrow Cu^{++} + 4\ NH_4^+ \quad (43)$$

$$Cd(NH_3)_4^{++} + 4\ H^+ \rightarrow Cd^{++} + 4\ NH_4^+ \quad (44)$$

When metallic iron is placed in a solution containing copper ion, the iron reacts with the copper ion to give metallic copper and ferrous ion.

$$Fe + Cu^{++} \rightarrow Cu\downarrow + Fe^{++} \quad (45)$$

The reaction of metallic iron with copper ion is an illustration of the facts of the electromotive series of the metals. The electromotive series is given on page 135. It consists of a list of the metals arranged in such a way that each metal will react with the ions of the metals below it in the list in the same way in which iron reacts with copper ion. Thus reference to the series shows that zinc, iron, magnesium and other metals should react with hydrogen ion (acids) to give hydrogen, while copper, being below hydrogen in the list, should not. Cadmium ion does not react with iron as easily as copper ion does, and the presence of acid in the solution prevents the reaction of cadmium ion and iron.

When the solution containing cadmium and ferrous ions is diluted and hydrogen sulfide is passed in, yellow cadmium sulfide is precipitated. Precipitation of the ferrous ion as ferrous sulfide is prevented by the acid present. The success of this test depends on how well other ions have been separated from cadmium ion. Copper and bismuth ions, if present, would give dark colored sulfides. If cadmium ion were absent, and stannic ion were present, the latter would give a yellow precipitate which could be mistaken for cadmium sulfide.

35. Precipitation of the Tin Group. When the solution containing the tin group in the form of ammonium thioarsenate, ammonium thioantimonate and ammonium thiostannate is made acid, the tin group sulfides are precipitated. On making the solution acid one would expect thio-acids to be formed. For example, in the case of arsenic the following reaction would be expected.

$$(NH_4)_3AsS_4 + 3\ HCl \rightarrow H_3AsS_4 + 3\ NH_4Cl \quad (46)$$

The thioarsenic acid, however, is unstable and decomposes into hydrogen sulfide and arsenic sulfide.

$$2\ H_3AsS_4 \rightarrow 3\ H_2S + As_2S_5 \quad (47)$$

The reactions for the antimony and tin compounds are similar to

this. It is to be noted that in all three sulfides the metals are in the higher state of oxidation, the formulas for the sulfides being As_2S_5, Sb_2S_5 and SnS_2, respectively.

36. Arsenic. Antimony and tin sulfides are dissolved by 12 *M* hydrochloric acid, while arsenic sulfide is not, because the concentration of the sulfide ion in a 12 *M* hydrochloric acid solution saturated with hydrogen sulfide is less than the sulfide ion concentration required to precipitate antimony and tin sulfides but greater than that required to precipitate arsenic sulfide. When antimonic sulfide, Sb_2S_5, reacts with hydrochloric acid, it loses two atoms of sulfur, and the compound formed is antimonous chloride.

$$Sb_2S_5 + 6\ HCl \rightarrow 2\ SbCl_3 + H_2S + 2\ S\downarrow \qquad (48)$$

On the other hand stannic sulfide, SnS_2, reacting with hydrochloric acid gives stannic chloride.

$$SnS_2 + 4\ HCl \rightarrow SnCl_4 + 2\ H_2S \qquad (49)$$

The dissolving of arsenic sulfide by ammonium hydroxide is another more complicated example of thio-salt formation in a basic solution. When the solution is again made acid the thio-salt is destroyed and the arsenic sulfide is reprecipitated.

37. Antimony. The precipitation of metallic antimony from solution by means of iron nails

$$2\ Sb^{+++} + 3\ Fe \rightarrow 3\ Fe^{++} + 2\ Sb\downarrow \qquad (50)$$

is similar to the precipitation of metallic copper by iron powder. As both tin and antimony are below iron in the electromotive series, one might expect the ions of both to react with the iron. This would happen in a solution in which the only positive ions were tin and antimony. The antimony is lower in the series and so would be precipitated first. After the antimony was nearly all out of solution the tin would begin to be precipitated. When a metal like iron is placed in a solution containing two or more different kinds of positive ions that are lower in the series, only one kind of ion reacts at a time and the different kinds of ions react in the inverse order of their positions in the series, the lowest first. The separation of antimony from tin by the iron nails takes place in an acid solution containing much hydrogen ion. In the electromotive series hydrogen ion comes between tin and antimony. Hence, in a solution containing tin, hydrogen, and

antimony ions the order of displacement is antimony, hydrogen, tin. Tin will not be displaced so long as there is a fairly large hydrogen ion concentration. However, under these conditions the tin is reduced from stannic ion, with a valence of four, to stannous ion, with a valence of two. This puts it in condition for the final test.

Metallic antimony will not react with the hydrogen ion of an acid to give hydrogen gas and antimony ion. Antimony can be changed into the ionic form by oxidation and so brought into solution. Nitric acid in the presence of hydrochloric acid is a convenient reagent for this purpose.[1]

$$Sb + HNO_3 + 3\ HCl \rightarrow SbCl_3 + NO + 2\ H_2O \qquad (51)$$

When the antimony ion is in solution it can be precipitated as antimony sulfide, giving the characteristic orange-colored precipitate.

38. Tin. The final test for tin ion, by adding mercuric chloride to a solution of stannous chloride, is precisely the same reaction as was employed as a test for mercury in the analysis of the copper group. There is only the difference that in the copper group the known substance, stannous chloride, was used to detect the unknown mercuric ion, while here the known mercuric chloride is used to detect the unknown stannous ion.

QUESTIONS

1. Make from memory an outline showing the separation and detection of all the ions of the hydrogen sulfide group, starting with the precipitation of the whole group. Quantities and concentrations of reagents and experimental details can be omitted.

2. Make an outline showing a simple method of separating one of each of the following pairs of ions from the other:

(a) Cu^{++} and Pb^{++}
(b) Pb^{++} and Cd^{++}
(c) Bi^{+++} and Sn^{++}
(d) Cu^{++} and As^{+++}
(e) As^{+++} and Sn^{++}

3. Complete and balance the following equations:

$Pb(NO_3)_2 + H_2SO_4 \rightarrow$
$Bi(NO_3)_3 + H_2SO_4 \rightarrow$
$Cu(NO_3)_2 + H_2SO_4 \rightarrow$
$Pb(C_2H_3O_2)_2 + K_2CrO_4 \rightarrow$
$Bi_2(SO_4)_3 + NH_4OH \rightarrow$
$CuSO_4 + NH_4OH \rightarrow$
$(NH_4)_3AsS_4 + HCl \rightarrow$
$(NH_4)_2SnS_3 + HCl \rightarrow$
$CuSO_4 + H_2S \rightarrow$
$Sb_2S_5 + (NH_4)_2S \rightarrow$
$SnS_2 + (NH_4)_2S \rightarrow$
$Cu(NH_3)_4SO_4 + HCl \rightarrow$

[1] Too much nitric acid in the mixture, or nitric acid alone, causes the formation of an insoluble antimonic acid.

4. Complete and balance each of the equations of Question 3 in the ionic form, writing the formulas for solid substances in the molecular form.

5. Complete and balance the following equations for oxidation-reduction reactions:

$CuSO_4 + Fe \rightarrow$ $\qquad$ $Bi(OH)_3 + Na_2SnO_2 \rightarrow$

$SnCl_2 + HgCl_2 \rightarrow$ $\qquad$ $SnCl_4 + Fe \rightarrow$

$SbCl_3 + Fe \rightarrow$ $\qquad$ $FeCl_3 + H_2S \rightarrow$

6. Write equations for the dissolving of antimonous and stannous sulfides, Sb_2S_3 and SnS, respectively, by ammonium polysulfide.

7. How do the properties of the copper-ammonia complex ion differ from the properties of copper ion?

8. Write the formulas for three complex ions.

9. What does the prefix "thio" mean? How is sodium thiosulfate, $Na_2S_2O_3$, related to sodium sulfate?

10. When the tin group sulfides are precipitated by making the solution acid after separating the tin group from the copper group, why are not stannic and antimonic sulfides dissolved by the acid solution?

11. Give an example from the hydrogen sulfide group procedure of an oxidation-reduction reaction. Point out which substance is oxidized and which is reduced.

12. What products would you expect from the reaction of copper sulfide and nitric acid if the reaction were a double decomposition reaction? What products are actually obtained?

13. Why does the reaction indicated by the equation

$$3\ Fe + 2\ Sb^{+++} \rightarrow 3\ Fe^{++} + 2\ Sb\downarrow$$

go in the direction indicated, but not from right to left?

14. What is meant by the electromotive (or displacement) series of the metals?

15. If copper comes below hydrogen in the electromotive series, what would you expect to happen when copper is placed in a hydrochloric acid solution?

16. If magnesium comes above hydrogen in the electromotive series, what would you expect to happen when magnesium is placed in a hydrochloric acid solution?

17. What is an amphoteric hydroxide? Write equations for the reaction of an amphoteric hydroxide with an acid and with a base.

18. What is required of the sulfide ion and metal ion concentrations in order that a metal sulfide can be precipitated?

19. What is the difference between the sulfides of the hydrogen sulfide group and those of the ammonium sulfide group which makes the separation of these two groups from each other possible?

20. What factors make the sulfide ion concentration small when the hydrogen sulfide group is being precipitated?

21. How would you prepare a solution of large hydrogen ion concentration?

CHAPTER VI

THE AMMONIUM SULFIDE GROUP

The ammonium sulfide group consists of ions which do not react with chloride ion or with sulfide ion in an acid solution to form precipitates, but which react with either hydroxide ion or sulfide ion in a basic solution to form hydroxide or sulfide precipitates. Outlines 7 and 8 show the method of precipitating and analyzing the group and the procedure is described in detail in Sections 39 and 40.

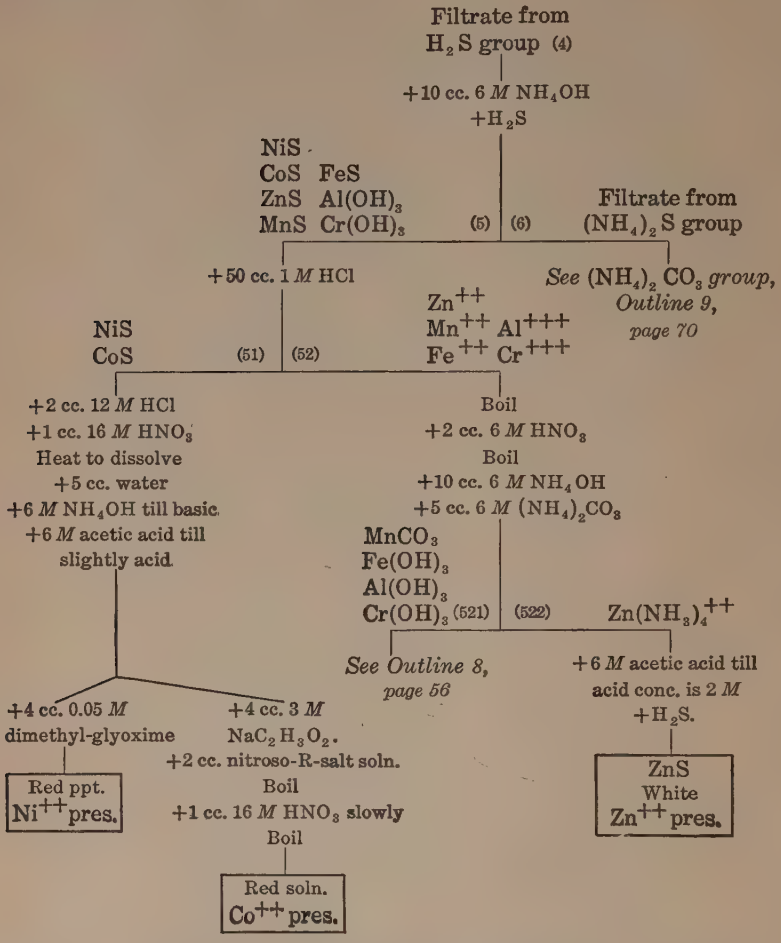
39. Precipitation of the Group. The ammonium sulfide group is to be precipitated from the filtrate from the hydrogen sulfide group. Ammonium sulfide is the group reagent, but instead of using a solution of ammonium sulfide, ammonium hydroxide and hydrogen sulfide are added. These react to form ammonium sulfide.

To the filtrate from the hydrogen sulfide group add 10 cc. of 6 *M* ammonium hydroxide and shake well. Test the solution with litmus. If it is not basic, add more ammonium hydroxide solution, 5 cc. at a time, till the solution is basic after it has been well mixed. A precipitate may be formed when the solution becomes basic; aluminum and chromium hydroxides are precipitated by ammonium hydroxide. Also any hydrogen sulfide left over from the precipitation of the previous group will be converted into ammonium sulfide and may partially precipitate some of the ions of the ammonium sulfide group.

The solution is now in condition for the addition of the hydrogen sulfide. Pass in hydrogen sulfide gas as in the precipitation of the hydrogen sulfide group, till after thorough shaking of the flask the gas inside will darken filter paper moistened with lead nitrate solution. If there is no precipitate, pass to the ammonium carbonate group, page 68, treating the solution as if it were the filtrate from the ammonium sulfide group.

If there is a precipitate, boil the mixture for about one minute. Test the solution with litmus. If it is not basic add 6 *M* ammonium hydroxide in 2 cc. portions till it is basic. Then filter,

in the ordinary way if the precipitate is small, or by suction if the precipitate is large. Wash the precipitate with a solution made by diluting 1 cc. of 6 *M* ammonium hydroxide to 100 cc. and passing in some hydrogen sulfide. The washings can be thrown away.



OUTLINE 7. Precipitation of the ammonium sulfide group and separation and detection of nickel, cobalt and zinc ions.

Test the filtrate for completeness of precipitation by adding 2 cc. of 6 *M* ammonium hydroxide and then more hydrogen sulfide. If there is no more precipitate, the solution can be set

aside till the ammonium carbonate group is to be precipitated. If there is a precipitate it must be filtered out and united with the first one for the treatment below. In this case the filtrate should be tested again for completeness of precipitation.

40. Analysis of the Group Precipitate. (*a*) *Nickel and Cobalt.* Transfer the precipitate to a casserole. The filter paper can be included if necessary. If the precipitate was washed into the casserole, decant all the water possible. Add 50 cc. of 1 *M* hydrochloric acid. Stir the mixture, remove the filter paper if it is present, and filter immediately. If there is a black residue it may be cobalt sulfide or nickel sulfide or both. The other sulfides, and a little of the cobalt and nickel sulfides are dissolved by the acid. Set the filtrate aside. Wash the precipitate once with water, rejecting the washings.

Wash the precipitate into a casserole and decant as much as possible of the water without loss of precipitate. Add 2 cc. of 12 *M* hydrochloric acid and 1 cc. of 16 *M* nitric acid. Heat till most of the black color disappears, showing that the sulfides have been dissolved. More of the mixed acid can be added if necessary. Boil the solution till the precipitated sulfur collects into a globule. Add 5 cc. of water. Add 6 cc. of 6 *M* ammonium hydroxide, and more if necessary, till the solution is slightly basic. Then add 6 *M* acetic acid in very small portions till the solution is *slightly* acid.

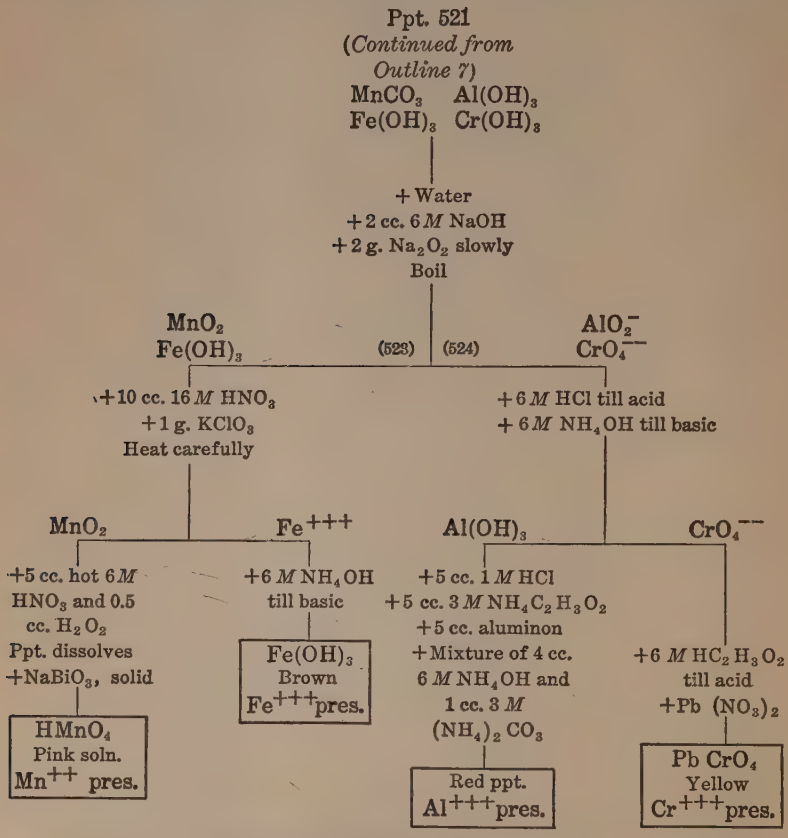
To about one quarter of the solution add 4 cc. of 0.05 *M* dimethyl-glyoxime [1] solution. A bright red precipitate shows the presence of nickel ion.

To another quarter of the slightly acid solution add 4 cc. of 3 *M* sodium acetate and 2 cc. of a 0.5 per cent nitroso-R-salt [2] solution and heat to boiling. Add 1 cc. of 16 *M* HNO_3, a little at a time, and keep near the boiling temperature for about a minute. If the solution is red at the end of this treatment the presence of cobalt ion is indicated. When the tests for nickel and cobalt ions are completed, the test portions and the remainder of the solution should be thrown away to avoid confusion.

(*b*) *Zinc.* The solution containing all the ions of the group except nickel and cobalt can now be treated further. Boil the solution for about half a minute to expel hydrogen sulfide, then

[1] Dimethyl-glyoxime is a carbon compound with the formula $C_4H_6N_2O_2H_2$.
[2] Nitroso-R-salt is a complex carbon compound.

add 2 cc. of 6 *M* nitric acid and heat to boiling again. Add 10 cc. of 6 *M* ammonium hydroxide and, if necessary, enough more in 2 cc. portions to make the solution basic. If the solution contains aluminum, chromium and ferric ions they will be precipitated as hydroxides. Add 5 cc. of 3 *M* ammonium carbonate. This will precipitate manganese carbonate. Filter and wash the precipitate with water, rejecting the washings. The precipitate is to be tested for manganese, ferric, aluminum, and chromic ions as described below. Acidify the filtrate with 6 *M* acetic acid, and in addition add a volume of 6 *M* acetic acid equal to half the volume of the solution, so as to make the solution 2 *M* with respect to acetic acid. Add a limited amount of hydrogen



Outline 8. Separation and detection of manganese, iron, aluminum and chromium ions.

sulfide gas. A white precipitate of zinc sulfide shows the presence of zinc ion.[1]

(*c*) *Separation of Aluminum and Chromium from Manganese and Iron.* Transfer the precipitate containing the aluminum, chromium and ferric hydroxides and manganese carbonate to a flask by perforating the filter paper and washing the precipitate from the paper with a stream of water from the wash bottle. Add 2 cc. of 6 *M* sodium hydroxide. Weight out 2 g. of sodium peroxide [2] and put it into a dry test tube. Cool the solution by holding it under running water and shaking. Then add the sodium peroxide a little at a time. Shake well after each addition and keep the solution cool. When all the sodium peroxide has been added, heat the solution to boiling and boil it for one minute. This is important, as the excess sodium peroxide, which is destroyed by boiling, would make trouble later if left in the solution. Dilute the solution to about 60 cc. If there is no appreciable residue left after the sodium peroxide treatment, manganese and iron ions are absent. If there is a residue, the presence of either manganese ion or ferric ion or both is indicated.

If there is no residue apparent, or if the amount of residue is too small to test, filter the solution through an ordinary filter paper, throw away the paper, and proceed to test the filtrate for aluminum and chromium ions as directed below. Filtering at this point is desirable because otherwise a small amount of ferric ion might give a test for aluminum ion later.

If there is an appreciable residue formed by the sodium peroxide treatment, filter it out on a hardened filter paper [3] by suction

[1] The white precipitate may turn greenish or gray as it stands, if the solution from which it was precipitated contained nickel or cobalt ion. Nickel and cobalt ions, if present in the ammonium sulfide group precipitate, will be present in traces in the solution tested for zinc ion. This is because small amounts of nickel and cobalt sulfides dissolve in the 1 *M* hydrochloric acid when they are being separated from the other ions of the group. If it is desired to test for traces of nickel and cobalt ions at this point, the zinc sulfide can be filtered out and the solution can be made basic with ammonium hydroxide and saturated with hydrogen sulfide. The black precipitate of nickel and cobalt sulfides can then be tested in a manner described above for nickel and cobalt tests.

[2] Sodium peroxide can be weighed on a piece of dry paper, but should not be handled on paper when there is any danger of water splashing on it. A little water on the sodium peroxide may set the paper on fire. This might happen without warning and cause a burn. Unused sodium peroxide should not be thrown into waste jars, but should be dissolved in water and thrown into the sink.

[3] Hardened filter paper is a specially prepared filter paper which will withstand contact with strong acid and base solutions better than ordinary filter paper. It is necessary to use hardened filter paper here because the solution to be filtered is strongly basic and because the next step requires that the paper come in contact with 16 *M* nitric acid.

and wash it with a little water. The residue may be a mixture of manganese dioxide and ferric hydroxide, while the filtrate may contain aluminum and chromium in the negative ions AlO_2^- and CrO_4^{--}, respectively. Set the filtrate aside for later analysis.

(*d*) *Manganese.* The next step is to separate the manganese dioxide from the ferric hydroxide and test for the manganese ion. Put the residue, with the filter paper, into a casserole and pour over it 10 cc. of 16 *M* nitric acid. Remove the paper by means of a glass rod and throw it away. Pour the solution, with the undissolved residue if there is any, into a test tube and put the test tube into a beaker partly full of boiling water. If necessary use some of the solution in the test tube to rinse the residue out of the casserole. When the contents of the test tube are hot, add about 0.3 g. of potassium chlorate. (Weigh out 1 g. and add a third of it, saving the remainder to be added later if necessary.) Stir with a stirring rod and heat for a minute or two. If there is no brown or black residue of manganese dioxide at this point, manganese ion is absent. In this case test the solution for ferric ion as described below, treating it as if it were the filtrate from the manganese dioxide residue.

If there is a brown or black residue after the addition of the potassium chlorate, add in small portions 0.7 g. more potassium chlorate and shake frequently. Then filter the mixture through an asbestos filter. To make an asbestos filter, set up the suction filter in the usual way, but without a filter paper. Put some asbestos fibers into a beaker, fill the beaker with water, stir up the mixture and filter through the funnel of the suction filter. If enough asbestos has been used, it will clog up the holes of the funnel and make a pad which will serve in place of a filter paper.

When the manganese dioxide residue is filtered, remove the filtrate and set it aside to be tested for iron. Wash the manganese dioxide once with water and throw away the wash solution. Heat 5 cc. of 6 *M* nitric acid in a test tube and mix with it 0.5 cc. of hydrogen peroxide solution. Pour this solution over the precipitate on the asbestos filter and apply the suction. The solution should dissolve some of the precipitate.

To the solution which has dissolved some of the precipitate add solid sodium bismuthate about 0.1 g. at a time, shaking well, till some of the solid remains undissolved. Let the solid settle. A pink or purple color in the solution shows the presence of

permanganate ion in this solution and is evidence of the presence of some ion of manganese in the original unknown.

(*e*) *Iron.* To the filtrate from the manganese dioxide add 30 cc. of 6 *M* ammonium hydroxide, and if necessary, enough more to make the solution basic. A reddish brown precipitate shows that ferric ion is present.

Iron in small quantities is a very frequent impurity in reagents as well as in unknowns. If ferric ion is found present, it is of interest to determine whether or not there is enough to consider it present in appreciable amount in the unknown. For this purpose the precipitate obtained may be compared with a similar precipitate obtained from a known amount of ferric ion. Measure out 1 cc. of 0.3 *M* ferric nitrate, or an equivalent amount of a ferric solution of any other concentration, and dilute it to 10 cc. Pour the solution into a beaker or flask and mix well. To 1 cc. of the solution add 35 cc. of water and 5 cc. of 6 *M* nitric acid. Then add 7 cc. of 6 *M* ammonium hydroxide and more if necessary to make the solution basic. Allow the solution to stand till a precipitate forms, and compare the amount of ferric hydroxide with the amount obtained in the other precipitate. The ferric hydroxide in the known solution represents between 1 and 2 mg. of iron. If the amount of precipitate obtained from the unknown is not much greater, it can be considered that only a very small amount of iron is present in the unknown.

(*f*) *Aluminum.* The filtrate resulting from the sodium peroxide treatment may contain aluminate and chromate ions. Add to it 6 *M* hydrochloric acid 5 cc. at a time till the solution is acid, then 6 *M* ammonium hydroxide 2 cc. at a time till it is basic, and finally 2 cc. of the ammonium hydroxide in excess. A white gelatinous precipitate may be aluminum hydroxide. It might also be silicic acid dissolved from the glass vessels by the strongly basic solution, or a metallic hydroxide present as the result of an incomplete separation. Filter off the precipitate and save the filtrate to test for chromate ion.

Pour over the precipitate on the paper 5 cc. of 1 *M* hydrochloric acid (made by mixing 5 cc. of 6 *M* acid and 5 cc. of water) and let the solution run through into a flask. The precipitate is dissolved by the acid solution and the filtrate contains the aluminum ion, if it is present. Add to the solution in the flask 5 cc. of 3 *M* ammonium acetate, mix well, then add 5 cc. of a 0.1

per cent solution of the ammonium salt of aurin tricarboxylic acid (also known as "Aluminon").[1] Finally add enough of a mixture of 4 cc. of 6 *M* ammonium hydroxide and 1 cc. of 3 *M* ammonium carbonate to either form a red precipitate or in the absence of a precipitate to turn the color of the solution orange or yellow. A red precipitate shows the presence of aluminum ion. Absence of a red precipitate shows that aluminum ion is absent. When the test is completed the solution and precipitate can be thrown away.

(*g*) *Chromium.* To the filtrate containing chromate ion add 4 cc. of 6 *M* acetic acid and enough more 1 cc. at a time to make the solution acid. If the solution is yellow, the presence of the chromate ion is indicated. This, of course, indicates that chromium ion, Cr^{+++}, was present in the filtrate from the hydrogen sulfide group, and that some chromium compound was present in the original sample. Add to the solution a drop or two of lead nitrate solution. A yellow precipitate confirms the presence of chromate ion.

Reactions of the Ammonium Sulfide Group

41. Precipitation. It has been mentioned above that certain ions, such as ferric ion, dichromate ion and permanganate ion, can react with sulfide ion to precipitate sulfur. In such reactions the sulfide ion is oxidized to sulfur and the other ions are reduced. Consequently, after the precipitation of the hydrogen sulfide group the elements iron, chromium and manganese if present will be present as ferrous, chromic and manganous ions, Fe^{++}, Cr^{+++} and Mn^{++}, respectively, regardless of which particular ions of these elements were present at the beginning.

In discussing the precipitation of the ammonium sulfide group it will simplify matters if it is assumed that the small amount of hydrogen sulfide which was present in the filtrate from the hydrogen sulfide group has escaped or has been driven out by boiling. When ammonium hydroxide is added, aluminum and chromium hydroxides are precipitated.

$$Al^{+++} + 3\ OH^- \rightarrow Al(OH)_3\downarrow \qquad (52)$$

Manganese, ferrous and cobalt ions do not react with the hydroxide ion of ammonium hydroxide, while zinc and nickel ions

[1] The reagent for aluminum, the ammonium salt of aurin tricarboxylic acid, is a complex carbon compound.

react with ammonia to form the complex ions $Zn(NH_3)_4^{++}$ and $Ni(NH_3)_4^{++}$ which remain in solution. When hydrogen sulfide is added, it reacts with ammonium hydroxide to form ammonium sulfide.

$$H_2S + NH_4OH \rightarrow (NH_4)_2S + 2\ H_2O \quad (53)$$

The sulfide ion of the ammonium sulfide reacts with the ferrous, manganous and cobalt ions to form ferrous, manganous and cobalt sulfides.

$$Fe^{++} + S^{--} \rightarrow FeS\downarrow \quad (54)$$

Aluminum and chromium hydroxides are not affected because aluminum and chromium sulfides are not formed in the presence of water. The reactions by which the complex ions are formed are reversible, and the complex ions are in equilibrium with small amounts of the simple ions and ammonia. When the simple ions, Zn^{++} and Ni^{++}, react with sulfide ion to form sulfide precipitates, the complex ions are completely broken up.

$$Zn(NH_3)_4^{++} \rightleftarrows Zn^{++} + 4\ NH_3 \quad (55)$$

$$Zn^{++} + S^{--} \rightarrow ZnS\downarrow \quad (56)$$

The reason why the sulfides of the ammonium sulfide group do not precipitate in the hydrogen sulfide group is that a larger concentration of sulfide ion is required for the precipitation of the former than for the precipitation of the latter. Hydrogen sulfide in solution is only slightly ionized and so gives only a small concentration of sulfide ion. The presence of a strong acid, such as hydrochloric acid, makes the sulfide ion concentration still less. When the hydrogen sulfide group is being precipitated, the sulfide ion concentration is too small to precipitate the ammonium sulfide group. When ammonium hydroxide and hydrogen sulfide are brought together, however, they react to form water and a salt, ammonium sulfide. The ammonium sulfide gives a sufficiently large concentration of sulfide ion to precipitate the ammonium sulfide group.

The use of ammonium hydroxide and hydrogen sulfide for the precipitation of the group requires a little more time and trouble than would the use of previously prepared ammonium sulfide. However, ammonium sulfide solutions are unstable in the presence of air. Oxygen reacts with sulfide ion to form sulfur.

$$2\ S^{--} + O_2 + 2\ H_2O \rightarrow 2\ S + 4\ OH^- \quad (57)$$

The presence of sulfur in the ammonium sulfide solution results in the formation of ammonium polysulfide. The progress of the reaction is indicated by the solution's slowly turning yellow. A yellow ammonium sulfide solution can be used for the precipitation of the group, but its use is objectionable when nickel ion is present.

If the colors of the precipitates of the ammonium sulfide group are kept in mind, helpful information as to the ions present can sometimes be obtained. Nickel, cobalt and ferrous sulfides are black. Zinc sulfide and aluminum hydroxide are white. Manganese sulfide is pink, or flesh-colored. Chromium hydroxide is gray-green. It is well to keep in mind the colors of some of the ions in solution also. Nickel ion is green, chromium ion is greenish blue, chromate ion is yellow, ferric ion is light yellow or brown, ferrous ion is light green, manganous ion is pale pink, and permanganate ion is pink to deep purple depending on the concentration. Most of the other ions encountered in the ammonium sulfide group are colorless.

42. Nickel and Cobalt. The fact that nickel and cobalt sulfides are not dissolved to any great extent by a dilute hydrochloric acid solution is useful for the separation of nickel and cobalt ions from the others. It might be expected that the sulfides would be dissolved by a dilute acid solution because they cannot be precipitated from such a solution. The probable reason why they are not dissolved is that the rate of dissolving is slow, so that very little of the sulfides can be dissolved in the time allowed. Nickel and cobalt sulfides can be dissolved easily if an oxidizing agent, such as nitric acid, is present.

The test for nickel by adding dimethyl-glyoxime must be carried out in a solution which has only a very small hydrogen ion concentration. Therefore the solution containing the nickel salt is made basic and then only slightly acid with acetic acid, which is a weak acid and gives much less hydrogen ion than hydrochloric acid. Dimethyl-glyoxime is a carbon compound having the composition $H_2O_2N_2C_4H_6$. The first two hydrogen atoms can be replaced by nickel giving a bright red precipitate.

$$H_2O_2N_2C_4H_6 + NiCl_2 \rightarrow NiO_2N_2C_4H_6\downarrow + 2\ HCl \qquad (58)$$

Dimethyl-glyoxime reacts with cobalt ion also, but the product is neither a precipitate nor colored, so the presence of cobalt ion

does not interfere with the test for nickel ion, provided enough of the reagent is used.

Cobalt ion can be tested for in the presence of nickel ion by the addition of another organic compound, nitroso-R-salt. The reaction of cobalt ion with the reagent to give the bright red compound is hindered by acids, so sodium acetate is added. The addition of sodium acetate reduces the acidity, or hydrogen ion concentration, of acetic acid. This is because a weak acid such as acetic acid is less ionized in the presence of one of its salts, such as sodium acetate, than it is in solution alone at the same concentration. Some other metallic ions will give a colored solution with nitroso-R-salt, but these colored compounds are destroyed by the addition of nitric acid, while the red color of the cobalt compound is not affected by the acid.

43. Zinc. The solution filtered from the cobalt and nickel sulfides contains the other ions of the group and small amounts of cobalt and nickel ions. It is boiled to remove the last traces of the hydrogen sulfide which is formed when the hydrochloric acid dissolves the sulfides.

$$ZnS + 2\ HCl \rightarrow ZnCl_2 + H_2S\uparrow \qquad (59)$$

Nitric acid is next added to oxidize the ferrous ion to ferric ion.

$$3\ Fe^{++} + NO_3^- + 4\ H^+ \rightarrow 3\ Fe^{+++} + NO + 2\ H_2O \qquad (60)$$

The reason why this is done is that next it is desired to precipitate all the ions except zinc ion by means of ammonium hydroxide and ammonium carbonate. Ferrous hydroxide would not be precipitated under these conditions. Ferric hydroxide, however, is precipitated by ammonium hydroxide along with aluminum and chromium hydroxides.

$$FeCl_3 + 3\ NH_4OH \rightarrow Fe(OH)_3\downarrow + 3\ NH_4Cl \qquad (61)$$

The manganese ion is precipitated by the addition of ammonium carbonate.

$$MnCl_2 + (NH_4)_2CO_3 \rightarrow MnCO_3\downarrow + 2\ NH_4Cl \qquad (62)$$

The zinc ion is not precipitated because it forms a complex ion with ammonia just as copper and cadmium ions do under similar conditions.

$$Zn^{++} + 4\ NH_3 \rightarrow Zn(NH_3)_4^{++} \qquad (63)$$

Small amounts of nickel and cobalt ions may be present in the filtrate along with the zinc ion. The test for zinc ion is made by acidifying the solution with acetic acid and adding hydrogen sulfide. A white precipitate of zinc sulfide indicates the presence of zinc ion.

44. Separation of Iron and Manganese from Aluminum and Chromium. Amphoteric Hydroxides. Aluminum hydroxide is amphoteric and like stannous hydroxide dissolves when an excess of sodium hydroxide is added. Amphoteric hydroxides ionize both as bases and acids. Aluminum hydroxide is slightly soluble in water, and the small amount of aluminum hydroxide in solution consists of the ions Al^{+++}, OH^-, H^+ and AlO_2^-, the last two being in equilibrium with the first two and with the solid as indicated by the following scheme:

$$\underbrace{Al^{+++} + 3\ OH^-} \rightleftharpoons \underbrace{AlO_2^- + H^+ + H_2O} \qquad (64)$$

$$\searrow\!\nwarrow\ Al(OH)_3\ (\text{solid})\ \nearrow\!\swarrow$$

When a reaction is at equilibrium, the removal of any one of the reacting substances will cause the reaction to go in the direction which will form more of the substance removed. The addition of a base will cause the removal of hydrogen ion, because hydrogen ion and hydroxide ion unite to form water.

$$H^+ + OH^- \rightarrow H_2O \qquad (65)$$

This will cause more hydrogen ion to be formed, and with it more aluminate ion, because this is formed along with hydrogen ion. Similarly the addition of an acid will remove hydroxide ion and cause the formation of aluminum ion, Al^{+++}, at the expense of the solid aluminum hydroxide and the aluminate and hydrogen ions. This explains the fact that aluminum hydroxide can be dissolved by either an acid or a strong base.

Chromium hydroxide can be made to go into solution in a sodium hydroxide solution also. It is believed, however, that the dissolving of chromium hydroxide is not analogous to that of aluminum hydroxide. The solution containing the apparently dissolved chromium hydroxide is a colloidal solution, that is, the chromium hydroxide is held in suspension in very fine particles rather than actually dissolved.

The formation of a colloidal solution of chromium hydroxide

is not a very satisfactory means of separating it from ferric hydroxide and manganese dioxide. Furthermore the subsequent separation of aluminum and chromium ions would not be convenient if this method were used. So the chromium hydroxide is oxidized to chromate ion, CrO_4^{--}, by means of sodium peroxide.

$$2\ Cr(OH)_3 + 3\ Na_2O_2 \rightarrow 2\ Na_2CrO_4 + 2\ NaOH + 2\ H_2O \quad (66)$$

At the same time manganese carbonate is oxidized to manganese dioxide, MnO_2.

$$MnCO_3 + Na_2O_2 \rightarrow MnO_2 + Na_2CO_3 \quad (67)$$

The manganese dioxide and the ferric hydroxide which is also present are only very slightly soluble and so can be separated by filtration from the sodium aluminate and the sodium chromate which are present in the solution.

The reactions of sodium peroxide with chromic hydroxide and manganese carbonate are reactions in which valence changes take place, oxidation-reduction reactions. Such reactions will be discussed more completely in Chapter XIV.

45. Manganese. When ferric hydroxide and manganese dioxide are treated with nitric acid, only the ferric hydroxide is dissolved. Manganese dioxide can be dissolved by nitric acid if the manganese is first reduced to the manganous state. Particles of filter paper and impurities in the nitric acid will reduce manganese dioxide to some extent. The part that is reduced and dissolved must be reoxidized and reprecipitated. For this purpose the potassium chlorate is added to the hot solution.

$$KClO_3 + HNO_3 \rightarrow HClO_3 + KNO_3 \quad (68)$$

$$2\ HClO_3 + Mn(NO_3)_2 \rightarrow MnO_2 + 2\ HNO_3 + 2\ ClO_2 \quad (69)$$

The potassium chlorate should be added a little at a time to avoid too rapid formation of chlorine dioxide. Chlorine dioxide is an explosive gas and is unpleasant to breathe. The mixture should be heated on a water bath so that the temperature will not become high enough to cause the chlorine dioxide to explode.

When the manganese dioxide has been filtered from the solution containing the ferric ion, it is dissolved by a warm solution of nitric acid and hydrogen peroxide. It is rather peculiar that hydrogen peroxide, an oxidizing agent, will reduce manganese

dioxide, another oxidizing agent. The peroxide can be thought of as supplying an atom of oxygen while the substance reduced supplies another to make molecular oxygen, O_2.

$$MnO_2 + H_2O_2 + 2\ HNO_3 \rightarrow Mn(NO_3)_2 + 2\ H_2O + O_2 \quad (70)$$

The effect of the sodium bismuthate is to oxidize the manganous ion to permanganate ion, MnO_4^-, which when present even in very small concentration gives a pink or purple color to the solution.

$$2\ Mn^{++} + 5\ BiO_3^- + 14\ H^+ \rightarrow 2\ MnO_4^- + 7\ H_2O + 5\ Bi^{+++} \quad (71)$$

46. Iron. The solution from which the manganese dioxide is filtered may contain ferric ion. If the solution is made basic with ammonium hydroxide, ferric ion will unite with hydroxide ion to form the reddish-brown slightly soluble ferric hydroxide. If desired the presence of ferric ion can be confirmed by adding hydrochloric acid to dissolve the precipitate, and then potassium ferrocyanide. This gives a precipitate of blue ferric ferrocyanide, $Fe_4[Fe(CN)_6]_3$, which is sometimes called "Prussian blue." Or, potassium or ammonium thiocyanate can be used. Thiocyanate ion gives a red solution if ferric ion is present.

47. Aluminum. The basic solution containing aluminate ion and chromate ion is made acid with hydrochloric acid. This changes aluminate ion to aluminum ion. Reference to Equation 64 and the explanation following it may help in understanding this change. The addition of hydrochloric acid removes some of the hydroxide ion, because the hydrogen ion of the acid unites with hydroxide ion to form water. If the hydroxide ion is removed from the left side of Equation 64, more aluminum ion will be formed by the dissolving of the solid when the system attempts to replace the hydroxide ion which was removed. The aluminum ion together with the chloride ion of the acid make aluminum chloride. The chromate ion at the same time undergoes a slight change, but one of minor importance for present purposes.

When ammonium hydroxide is added, aluminum hydroxide is precipitated, and the chromate ion remains in solution,

$$Al^{+++} + 3\ OH^- \rightarrow Al(OH)_3\downarrow \quad (72)$$

48. Chromium. The test for chromate ion involves the same reaction as the test for lead ion in the analysis of the chloride

group. In this case, however, the lead ion is the known substance, while the chromate ion is the unknown. Lead ion unites with chromate ion to give a precipitate of yellow lead chromate.

QUESTIONS

1. Make from memory an outline showing the separation and detection of all the ions of the ammonium sulfide group, starting with the precipitation of the group. Quantities and concentrations of reagents and experimental details may be omitted.

2. Make an outline showing a simple method of separating one ion of each of the following pairs from the other:

(a) Al^{+++} and Cr^{+++}
(b) Al^{+++} and Zn^{++}
(c) Cr^{+++} and Mn^{++}
(d) Ni^{++} and Fe^{+++}
(e) Cr^{+++} and Fe^{+++}

3. Write equations in both the ionic and the molecular form for the reactions taking place when 1 *M* hydrochloric acid is added to the ammonium sulfide group precipitate.

4. Write equations in both the ionic and the molecular form for the reactions taking place when ammonium hydroxide is added to the solution containing aluminum, chromium, ferric, manganese and zinc ions. Include the equation for the reaction involving the zinc ion.

5. Explain how aluminum hydroxide can react with either a hydrochloric acid solution or a sodium hydroxide solution.

6. Write equations 69 and 70 in the ionic form.

7. Write equations in both the ionic and the molecular form for two tests for ferric ion.

8. Write equation 72 in the molecular form.

9. Write ionic equations showing the changes which take place when a solution containing aluminate ion is made acid by adding hydrochloric acid and then is made basic with ammonium hydroxide.

10. Give formulas for some other ions containing the elements iron, chromium and manganese besides ferrous, chromic and manganous ions, respectively.

11. What would happen to copper ion if it were present in the filtrate from the hydrogen sulfide group when the ammonium sulfide group was being precipitated?

12. Explain the fact that in the final test for zinc ion the zinc sulfide is precipitated in an acid solution while it would not precipitate in the hydrogen sulfide group.

13. Why will boiling a solution free it from a dissolved gas?

14. If the ammonium sulfide group precipitate consisted of 0.5 g. of zinc sulfide and nothing else, how much 1 *M* hydrochloric acid would be required to dissolve it? Ans. 10.2 cc.

CHAPTER VII

THE AMMONIUM CARBONATE GROUP

The ammonium carbonate group consists of metallic ions which are not precipitated in the first three groups and which can be precipitated by ammonium carbonate in a solution containing a large proportion of alcohol. The method of precipitation and the analysis of the precipitate are shown in Outline 9 and are described in detail in Sections 49–51.

49. Preparation of the Solution. The filtrate from the ammonium sulfide group contains the ions of the ammonium carbonate and alkali groups. It also contains considerable quantities of ammonium salts and various sulfur compounds and may contain small quantities of ions of the ammonium sulfide group which faulty manipulation has failed to remove. It is desirable to remove all of the last three classes of materials before attempting to precipitate the ammonium carbonate group.

Place the filtrate from the ammonium sulfide group in a beaker and evaporate the solution. Often a precipitate will appear before the solution is half evaporated. This precipitate is usually free sulfur or a mixture of sulfur and sulfides of metals of the ammonium sulfide group. Continue the boiling till the precipitate is coagulated sufficiently to be readily removed by filtration. Then filter, reject the precipitate and continue the evaporation of the filtrate. When the volume of the solution has been reduced to 50 cc. or less, transfer the solution to a porcelain casserole or evaporating dish of about 75 cc. capacity and continue the evaporation. Just before the contents of the casserole become dry they often spatter. When this happens, remove the flame till spattering ceases. Place the casserole, supported by a clay or nichrome triangle on a ring stand, within a half inch of the opening of the fume duct, or under a hood. This is to avoid polluting the laboratory with fumes of sublimed ammonium salts which are copiously given off during the remainder of the process. Continue heating carefully, increasing the heat when spattering ceases and finally heat till the smoke of

ammonium salts stops coming off. If desired, the burner can be inverted and the mass can be heated from the top. This will minimize spattering and make the process more rapid. It can be determined whether or not the ammonium salts are all expelled by removing the flame and observing whether or not the white smoke continues to arise from the hot dish.

When the process is finished, allow the casserole to cool so that it will not be cracked by contact with cool liquids. Then add 5 cc. of 6 *M* hydrochloric acid and heat. If a solid residue adheres to the casserole, rub it loose with a stirring rod. Evaporate to the point where spattering begins, or to dryness if the quantity of residue is small.

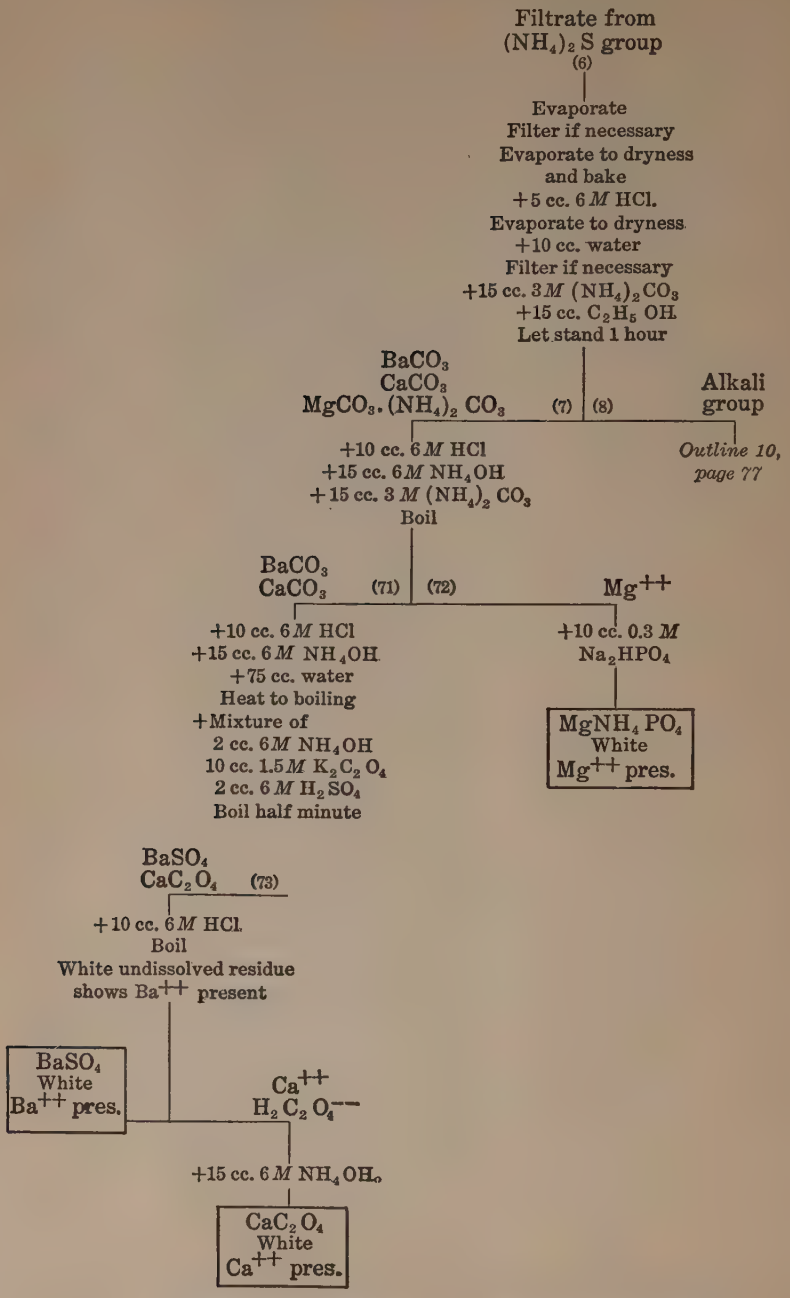
At this point examine the residue in the casserole. If there is no residue left, ions of the ammonium carbonate and alkali groups are absent and the analysis is finished as far as the metallic ions are concerned.

If the residue is any color other than clean white, ions of the ammonium sulfide group are probably present, and the task of precipitating this group must be repeated. To do this, dissolve the residue in 5 cc. of 6 *M* hydrochloric acid and some water. When the solid residue is dissolved, treat the resulting solution as a filtrate from the hydrogen sulfide group.

If the residue is a clean white color, any or all of the ions of the ammonium carbonate and alkali groups may be present. Dissolve the residue in 10 cc. of water. If necessary stir and warm the mixture to hasten the dissolving process. Filter out and reject any insoluble residue. Treat the solution as described in the next paragraph for the precipitation of the ammonium carbonate group.

50. Precipitation of the Ammonium Carbonate Group. To the 10 cc. of solution obtained as described above, add 15 cc. of 3 *M* ammonium carbonate and 15 cc. of denatured alcohol. Shake and let stand an hour, or, better, till the next laboratory period. Then filter, using suction if the precipitate is large. The precipitate may contain the carbonates of any or all of the metals of the ammonium carbonate group, while the filtrate may contain sodium and potassium ions. The filtrate should be reserved for the analysis of the alkali group.

After pouring the solution and precipitate into the filter, it may be found that some of the precipitate adheres to the inside



OUTLINE 9. Precipitation and analysis of the ammonium carbonate group.

of the flask. In such a case, that portion of the precipitate can be left in the flask till the precipitate is to be analyzed. Then it can be dissolved by means of hydrochloric acid and the same hydrochloric acid solution can be used for dissolving the main portion of the precipitate as described in the next paragraph. If the precipitate is to be preserved for any length of time before it is to be analyzed, it can be conveniently preserved on the paper in the flask in which it was precipitated.

51. Analysis of the Group Precipitate. (*a*) *Magnesium.* Dissolve the ammonium carbonate group precipitate by adding to it 10 cc. of 6 *M* hydrochloric acid. If the precipitate is on a filter, the acid can be poured into the filter, caught in a test tube or flask as it comes through the filter and returned a second time to the filter to dissolve the remainder of the precipitate. To the solution containing the ions of the ammonium carbonate group add 15 cc. of 6 *M* ammonium hydroxide and 15 cc. of 3 *M* ammonium carbonate and heat to boiling. This will precipitate barium and calcium carbonates, but without the addition of alcohol magnesium ion will remain in solution. Filter, and to the filtrate add 10 cc. of 0.3 *M* sodium phosphate, Na_2HPO_4. A white precipitate shows the presence of magnesium ion. If a precipitate is not formed immediately, allow the solution to stand for a while before throwing it away.

(*b*) *Barium.* Dissolve the precipitate of barium and calcium carbonates by pouring through the filter 10 cc. of 6 *M* hydrochloric acid. Pour the acid through more than once if necessary. Catch the filtrate in a beaker and add 15 cc. of 6 *M* ammonium hydroxide and 75 cc. of water. The solution should be basic. Heat to boiling. In a test tube mix 2 cc. of 6 *M* ammonium hydroxide, 10 cc. of 1.5 *M* potassium oxalate and 2 cc. of 3 *M* sulfuric acid. Add the solution slowly to the boiling solution containing the barium and calcium ions, pouring it down the side of the beaker and stirring continuously. Barium sulfate and calcium oxalate are precipitated. Absence of any precipitate shows the absence of both barium and calcium ions, in which case the analysis of the ammonium carbonate group is complete. If there is a precipitate, boil the mixture for a half minute, then filter it, rejecting the filtrate. Wash the precipitate with water, rejecting the washings. Then wash the precipitate into a flask and add 10 cc. of 6 *M* hydrochloric acid. Mix well and heat to

boiling. The hydrochloric acid will dissolve the calcium oxalate but will not dissolve the barium sulfate. If a white precipitate remains undissolved, it is barium sulfate, which shows the presence of barium ion. The solution contains the calcium ion. Filter and test the filtrate for calcium ion as directed below.

If desired, the barium sulfate may be further tested by a flame test. Heat one end of a clean platinum or nichrome or other heat-resisting wire in a colorless flame till any traces of impurities which impart a color to the flame are burned off. Then take on the end of the wire a small amount of the precipitate to be tested and heat again. Barium compounds impart a persistent green color to a flame.

(*c*) *Calcium.* To the filtrate containing calcium ion add 15 cc. of 6 *M* ammonium hydroxide and more if necessary to make the filtrate basic. A white precipitate of calcium oxalate shows the presence of calcium ion.

Reactions of the Ammonium Carbonate Group

52. Evaporation to Dryness. The sulfur present in the filtrate from the ammonium sulfide group may be present as free sulfur or in the form of sulfide or polysulfide ion. Boiling the solution boils out ammonium sulfide and decomposes the polysulfide ion leaving free sulfur. Sufficient boiling coagulates free sulfur so that it can be removed by filtration. If the solution is colored when the polysulfide ion has been decomposed and the sulfur has been filtered out, the color is evidence that ammonium sulfide group ions are still present.

By baking the residue that remains after evaporating the filtrate from the ammonium sulfide group to dryness, all ammonium salts are removed. Ammonium salts are formed whenever ammonium hydroxide neutralizes an acid, or whenever an acid neutralizes ammonium hydroxide. When solid ammonium salts are heated, they pass directly from the solid to the vapor state without going through the liquid state. Such a change from the solid to the vapor state is called sublimation. Besides ammonium salts, many compounds of mercury, arsenic and antimony sublime more or less easily. Baking will remove any of these latter compounds if they happen to be present. The purpose of the process of evaporation to dryness is to eliminate everything that might interfere with the precipitation and analysis of the ammonium carbonate group.

When the residue has been baked, it is treated with hydrochloric acid. Heating partially decomposes some calcium and magnesium compounds leaving oxides which are sparingly soluble in water. These are converted to soluble chlorides by the action of hydrochloric acid.

53. Precipitation. When a solution containing magnesium, barium and calcium ions is treated with ammonium carbonate and alcohol, barium and calcium carbonates and a double carbonate of magnesium and ammonium are precipitated.

$$BaCl_2 + (NH_4)_2CO_3 \rightarrow BaCO_3\downarrow + 2\ NH_4Cl \quad (73)$$

$$MgCl_2 + 2\ (NH_4)_2CO_3 \rightarrow MgCO_3\cdot(NH_4)_2CO_3\downarrow + 2\ NH_4Cl \quad (74)$$

In the precipitation of the group, the volume of the solution is kept small so that the ammonium carbonate concentration will be large and the amount of barium, calcium and magnesium carbonates retained in the filtrate will be reduced to a minimum. If there is considerable ammonium ion in the solution and the addition of the alcohol is omitted, the magnesium ion is not precipitated, while barium and calcium ions are precipitated as carbonates. This fact is used in the separation of magnesium ion from barium and calcium ions after the group precipitate has been dissolved by hydrochloric acid.

54. Analysis. Carbonates generally react with acids, giving off carbon dioxide gas. The ammonium carbonate group precipitate can be dissolved easily by hydrochloric acid.

$$BaCO_3 + 2\ HCl \rightarrow BaCl_2 + H_2O + CO_2\uparrow \quad (75)$$

It can be considered that carbonic acid, H_2CO_3, is first formed, as would be expected if the reaction were a simple double decomposition. The carbonic acid breaks down into water and carbon dioxide, which, having only a limited solubility, escapes from the solution.

$$H_2CO_3 \rightarrow H_2O + CO_2\uparrow \quad (76)$$

Magnesium ion can be detected by adding sodium phosphate to the solution from which the barium and calcium ions have been removed. If the solution is basic and if ammonium ion is present, magnesium ammonium phosphate is precipitated.

$$Mg^{++} + NH_4^+ + PO_4^{---} \rightarrow MgNH_4PO_4\downarrow \quad (77)$$

The simultaneous addition of sulfate and oxalate ions to a solution containing barium and calcium ions gives a precipitate of barium sulfate and calcium oxalate.

$$BaCl_2 + (NH_4)_2SO_4 \rightarrow BaSO_4\downarrow + 2\ NH_4Cl \qquad (78)$$

$$CaCl_2 + K_2C_2O_4 \rightarrow CaC_2O_4\downarrow + 2\ KCl \qquad (79)$$

It is interesting to note that if only sulfate ion is added to the above solution, both barium and calcium ions will precipitate as sulfates; if only oxalate ion is added, both ions precipitate as oxalates; while if sulfate ion and oxalate ion are added together, barium ion precipitates as sulfate and calcium ion precipitates as oxalate. The reason is that barium sulfate is less soluble than barium oxalate, while calcium oxalate is less soluble than calcium sulfate.

When hydrochloric acid is added to the precipitate composed of barium sulfate and calcium oxalate, only the latter is dissolved.

$$CaC_2O_4 + 2\ HCl \rightarrow CaCl_2 + H_2C_2O_4 \qquad (80)$$

The fact that barium sulfate is unaffected by the same reagent that dissolves calcium oxalate is in harmony with the generalized observation that slightly soluble salts of weak acids tend to be dissolved by strong acids, while salts of strong acids are not so affected. Weak acids are only slightly ionized in water solution while strong acids are nearly or completely ionized under the same conditions. In the analysis of this and previous groups, those precipitates which are sulfides or carbonates, salts of weak acids, are formed only in basic or weakly acid solutions and are generally dissolved by strong acids, such as hydrochloric acid or nitric acid. The precipitates which are salts of strong acids, such as chlorides or sulfates are not readily dissolved by any acid, strong or weak.

When calcium oxalate has been dissolved, as indicated in Equation 80, and has been separated from the solid barium sulfate by filtration, calcium ion is reprecipitated by making the solution basic with ammonium hydroxide. The ammonium hydroxide neutralizes both the hydrochloric acid and the oxalic acid present. Oxalic acid and ammonium hydroxide form ammonium oxalate, which in neutral or basic solution readily precipitates calcium ion as calcium oxalate.

A fuller discussion of the forming and the dissolving of precipitates is given in Chapter XIII.

QUESTIONS

1. Make from memory an outline showing the separation and detection of all the ions of the carbonate group. Quantities and concentrations of reagents and experimental details may be omitted.

2. By means of an outline show how each of the following pairs of ions might be separated in a simple manner: (a) calcium and magnesium, (b) barium and iron, (c) barium and lead, (d) manganese and magnesium.

3. Write equations for all the reactions taking place in the precipitation and analysis of the ammonium carbonate group.

4. What was the origin of the ammonium salts mentioned as being present in the filtrate from the ammonium sulfide group? Write equations to illustrate.

5. What color is given to solutions by ions of the carbonate and alkali groups?

6. Which positive ions in the whole analytical scheme are colored in solution?

7. What conclusion could be drawn if one had a colored solution at the point where ammonium carbonate solution is added? What should be done in such a case?

8. What ions are formed when the double salt $MgCO_3 \cdot (NH_4)_2CO_3$ is placed in solution?

9. Is it likely that lead sulfate and silver chloride could be dissolved by nitric acid?

10. Lead chromate can be dissolved by nitric acid. Is chromic acid weaker or stronger than nitric acid?

11. The solubility in water of calcium carbonate is 0.013 g. per liter and that of calcium sulfate is 2.4 g. per liter. What would be the formula of the precipitate formed if calcium ion were added to a solution containing considerable of both carbonate and sulfate ions? What salts might be used in performng the fore going experiment?

CHAPTER VIII

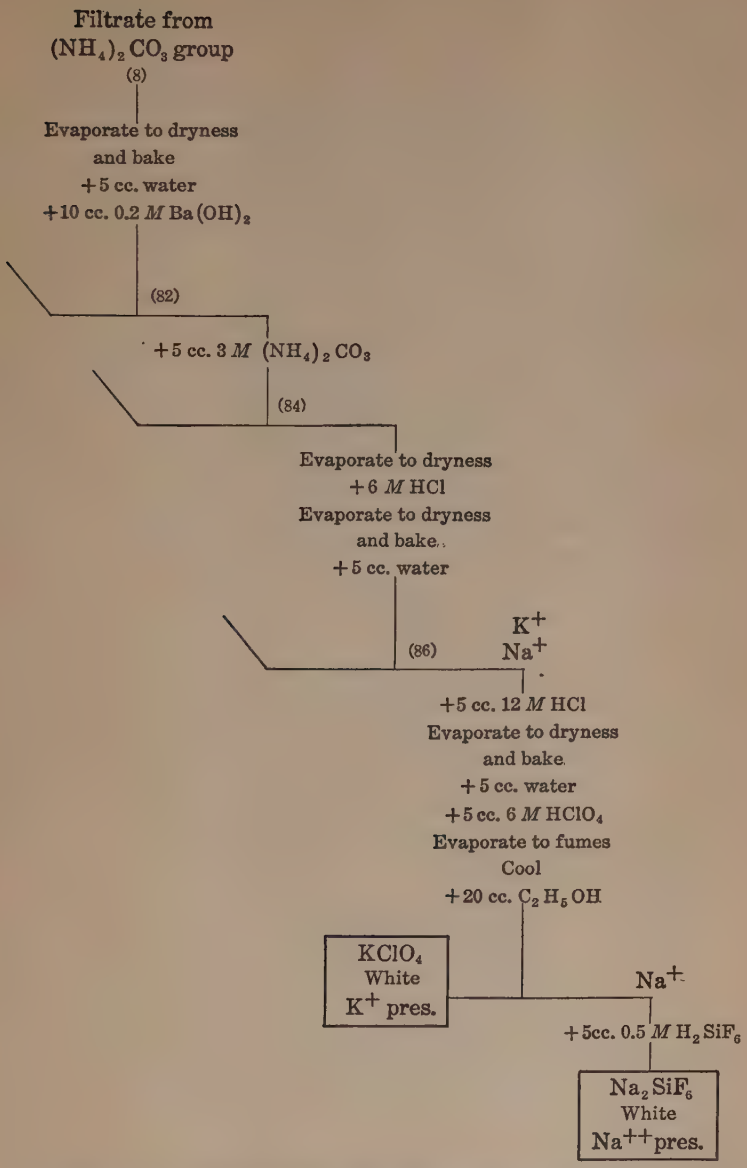
THE ALKALI GROUP

The alkali group consists of all those ions which are not precipitated in any of the other groups, namely potassium, sodium and ammonium ions. The alkali group is not precipitated as a group as are the other groups. The filtrate from the ammonium carbonate group cannot be used to test for the ammonium ion because this ion has been necessarily added to the sample in the analysis of the previous groups. Further, ammonium ion as well as the metallic ions of all the other groups must be completely removed before testing for potassium and sodium ions, because the presence of these other ions interfere with the test. Hence the analysis of the alkali group consists in the removal of all positive ions except potassium and sodium and in testing for these two latter ions in the remaining residue.

55. Preparation of the Solution. The filtrate from the carbonate group is used for testing for potassium and sodium ions. Evaporate the filtrate from the carbonate group to dryness and bake. During the evaporation the vapors given off may contain enough alcohol to catch fire. So long as the flame is only a few inches high no particular harm is done. It is well to remove the bunsen flame while the vapors burn. If the flame of the burning vapor becomes too high, both the fire hazard and the danger of breaking the dish are much increased. The flame can be extinguished by placing a watch glass over the porcelain dish.

The object of baking is to remove ammonium salts, which if not removed, would seriously interfere with the test for potassium ion. If no residue remains after baking, sodium and potassium ions are absent, and the analysis is finished.

After baking and allowing the dish to cool, add 5 cc. of water and by warming the water and rubbing the residue into small pieces with a stirring rod get a maximum portion dissolved. Then without filtering add 10 cc. of 0.2 *M* barium hydroxide to the hot liquid, stir and filter, rejecting the precipitate. To the filtrate add 5 cc. of 3 *M* ammonium carbonate, or enough to



OUTLINE 10. Separation and detection of potassium and sodium ions.

precipitate all the barium ion, and heat the solution to boiling, after which let it stand for about 5 minutes. Then filter again and reject the precipitate.

Evaporate the filtrate to dryness. Moisten the residue with 6 *M* hydrochloric acid, evaporate to dryness again and bake. If no residue remains either before or after baking, potassium and sodium ions are absent. If a residue remains, add 5 cc. of water, stir well, and filter to remove any undissolved residue. Reject the residue, but save the filtrate.

To the filtrate add 5 cc. of 12 *M* hydrochloric acid and evaporate to dryness and bake again. If no residue remains at this point, potassium and sodium ions are absent. If a white residue remains it may be potassium chloride or sodium chloride or both. If there is a white residue, dissolve it in 5 cc. of water and test the solution for potassium and sodium ions as described below. The procedure up to this point has had for its purpose the elimination of all metallic ions except those of potassium and sodium, and the elimination of all negative ions except chloride ion.

56. Potassium. To test for potassium ion add 5 cc. of 6 *M* perchloric acid to the solution from the last treatment, evaporate the solution in a beaker till heavy white fumes of perchloric acid are copiously given off, and then cool the vessel nearly to room temperature. On cooling, a solid residue often forms, but whether the contents of the vessel are solid or liquid at this point add 20 cc. of denatured alcohol. If the residue was solid rub it loose and stir for about 3 minutes. (*Caution: do not heat the solution.*) [1] An undissolved white residue is potassium perchlorate, and is a sufficient test for potassium. If there is no white residue, potassium ion is absent.

57. Sodium. Filter off the potassium perchlorate and to the filtrate add 5 cc. of 0.5 *M* fluosilicic acid. If potassium ion was absent, the filtration can be omitted, of course. A slimy white precipitate of sodium fluosilicate indicates the presence of sodium ion. If in doubt as to whether or not a given precipitate is heavy enough to warrant the assumption that sodium ion is present, mix in a beaker 1 cc. of 0.5 *M* magnesium nitrate with 15 cc. of alcohol, then add 3 cc. of 0.5 *M* fluosilicic acid. If the white precipitate in the unknown solution is decidedly heavier than

[1] After adding alcohol to the solution containing perchloric acid never heat the solution. This mixture may explode if heated.

that in the solution known to contain magnesium nitrate, it can be assumed that sodium ion is present.

58. Test for Ammonium Ion. The test for ammonium ion is made on a separate portion of the original sample and not on the filtrate from the carbonate group. The test consists in adding to a portion of the unknown material sodium hydroxide solution and determining the presence or absence of ammonia by smelling the gas above the solution.

If the sample is a solid, place about 0.2 g. of the finely powdered sample in a beaker. If it is a liquid place about 5 cc. of the liquid in a beaker. In either case add to the sample 10 cc. of 6 *M* sodium hydroxide. Shake or stir and then *cautiously* smell the vapors given off. The odor of ammonia is a sufficient test for the presence of ammonium ion in the sample. If no odor of ammonia is perceived, warm the beaker, smelling of it from time to time till the odor of ammonia is noted, or till the solution is about as hot as the skin of the hands will tolerate. Do not boil the solution, as steam interferes with the test.

In case of doubt as to whether or not the odor of ammonia is perceived, the following supplementary experiment is suggested. To 100 cc. of water add 1 cc. of 3 *M* ammonium chloride and mix thoroughly. This forms an approximately 0.03 *M* solution of ammonium chloride. Thoroughly wash the measuring vessel if it is to be used in the next operation. Place in a beaker 5 cc. of the 0.03 *M* ammonium chloride and make the above test for ammonium ion on this sample. If the odor of ammonia in the unknown is not equal to or greater than the odor in this "control" test, ammonium ion may be considered absent in the unknown.

Never try to smell the contents of a beaker in the hands of another person. Take the beaker in your own hand, and always smell cautiously at first.

Reactions Used in Testing for Potassium, Sodium, and Ammonium

59. Preparation of the Solution. The first object in the procedure for potassium and sodium ions was to eliminate everything that would interfere with the potassium and sodium ion tests. This means the elimination of all positive ions except potassium and sodium ions and of all negative ions except chloride

ion. Evaporation to dryness and baking, if carefully done, will eliminate all ammonium salts, any free acids present, any volatile salts, and often will decompose salts of the heavy metals into their oxides. Most of the latter are soluble to only a slight extent.

The addition of barium hydroxide serves two purposes: first, the hydroxide ion will precipitate magnesium ion or other metallic ions as hydroxides and second, the barium ion will precipitate any sulfate ion that may be present. The addition of ammonium carbonate solution has for its purpose the removal of the excess barium ion by precipitation. By boiling the solution after the addition of ammonium carbonate, the precipitate is coagulated and is less apt to pass through the filter.

The two treatments with 12 *M* hydrochloric acid are for the purpose of eliminating negative ions other than chloride ion. This process of changing a metallic salt of one acid to the corresponding salt of a second acid by repeated evaporation to dryness after adding the second acid is one that is often used in analytical work. It is sometimes spoken of as "fuming off." As the result of the fuming off process used here, potassium and sodium chlorides are the only substances left.

60. Potassium. By evaporating the perchloric acid solution till heavy fumes are evolved, hydrochloric acid is eliminated by the fuming off process, and potassium and sodium chlorides are changed to potassium and sodium perchlorates, respectively. After this, potassium ion can be separated from sodium ion, because of the fact that potassium perchlorate is only slightly soluble in alcohol while sodium perchlorate is freely soluble in this solvent.

61. Ammonium Ion. Because ammonium ion forms no slightly soluble compounds which lend themselves to use in a scheme of analysis, and also because ammonium ion is frequently added in the course of the analysis, provision is made for its detection by an individual test outside the scheme of analysis. The test is based on the fact that ammonium salts when placed in a basic solution give ammonia gas out into the air. Ammonia can be recognized by its odor.

$$NH_4^+ + OH^- \rightleftharpoons NH_3\uparrow + H_2O \qquad (81)$$

QUESTIONS

1. Make from memory an outline showing the separation and detection of the ions of the alkali group. Quantities and concentrations of reagents and experimental details may be omitted. Omit also the preparation of the solution.

2. Why is the test for ammonium ion not made on the filtrate from the ammonium carbonate group? Distinguish between ammonia and ammonium.

3. Write an equation for the reaction of sodium chloride and perchloric acid. Is this reaction reversible? How can it be made to go to completion?

4. What kinds of materials may be removed from a solution by means of the fuming off process? How can sodium chloride be changed to sodium nitrate? Is the fuming off process used anywhere in the scheme of analysis besides in the analysis of the alkali group?

5. Write molecular equations for the reactions that would be used in showing that ammonium ion was present in a solution of ammonium sulfate.

CHAPTER IX

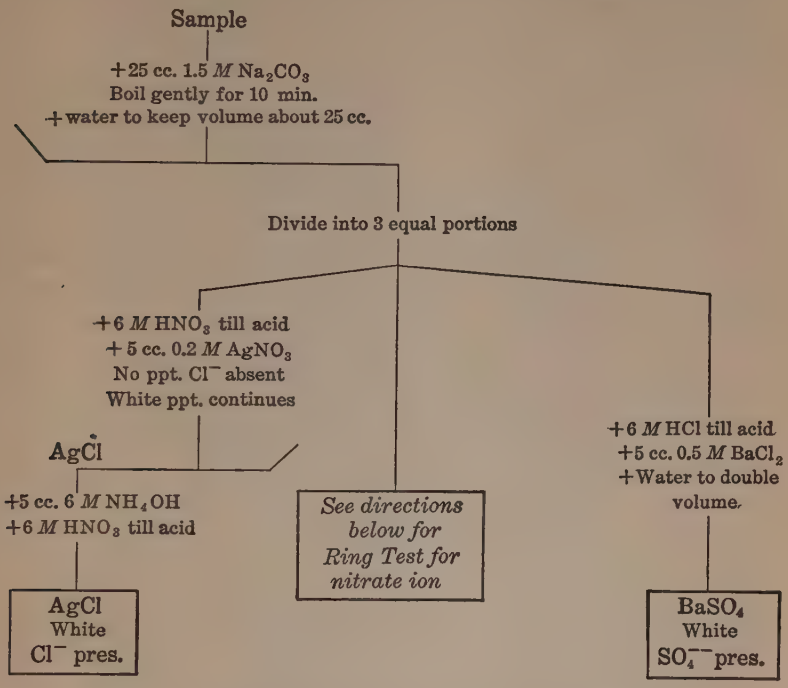
THE DETECTION OF NEGATIVE IONS

The negative ion of a compound is as important as the positive ion. However the number of negative ions frequently met in the laboratory and in the materials of daily life is much less than the number of positive ions similarly met. There is no well ordered scheme of analysis for negative ions comparable with the schemes used for positive ion analysis. In view of these facts and in view of the time limitations of a beginning course, methods are given for the detection of only a few of the more common negative ions.

62. Quantity of Sample. The quantity of sample used in the detection of negative ions should be large enough to give positive tests. If the unknown is a solid that can be dissolved by water or acids, a half gram or less is sufficient for making the tests for chloride, nitrate, and sulfate ions. About one tenth gram will be needed for each of the other tests. If the unknown substance is a solution, the samples taken for analysis, as with solids, should be large enough to give decisive tests. One way to learn this would be to place 10 cc. of the solution in a small weighed beaker, evaporate the solution to dryness and weigh the residue. From this it would be easy to compute the volume of unknown solution containing the required weight of the dissolved solid. In practice it is usually more expeditious to try using from 10 to 20 cc. of the solution for the chloride, nitrate and sulfate tests, and to use from 1 to 5 cc. for each of the other tests. Trial will usually show whether too much, too little, or enough of the liquid sample is being used.

63. Procedure for Chloride, Nitrate, and Sulfate Ions. (*a*) *Precipitation of Metallic Ions.* To a sample of suitable size, either solid or liquid, add 25 cc. of 1.5 *M* sodium carbonate solution and boil for ten minutes. From time to time add water so that the final volume will not vary greatly from the original volume of the solution. If a precipitate has formed, or if a residue remains after boiling, filter the solution and reject the

solid material left on the filter. The filtrate now contains the negative ions in solution. It has a basic reaction toward litmus because it contains portions of the sodium carbonate not used in



Outline 11. Procedure for chloride, nitrate and sulfate ions.

forming the precipitate. Divide the filtrate into three approximately equal portions. Each portion is to be used for testing for one of the three negative ions.

(*b*) *Test for Chloride Ion.* To the first portion add 6 *M* nitric acid till the solution after stirring is acid to litmus. Then add 5 cc. of 0.2 *M* silver nitrate solution. If no precipitate forms, chloride ion is absent, and the solution can be rejected. If a white precipitate forms it may be silver chloride, indicating the presence of chloride ion. To confirm the presence of chloride ion, filter and reject the filtrate. Wash the precipitate with water and reject the wash water. Slowly pour over the precipitate on the filter 5 cc. of 6 *M* ammonium hydroxide catching the liquid in a clean test tube. To the solution in the test tube add

6 *M* nitric acid till the solution is acid to litmus after stirring. The presence of a white precipitate indicates the presence of chloride ion.

(*c*) *The Ring Test for Nitrate Ion.* To a separate 5 cc. portion of the filtrate from the sodium carbonate treatment add 3 *M* sulfuric acid till the solution is acid to litmus. Pour the solution thus formed into a test tube to a depth of about 2 cm. Then add an equal volume of 0.5 *M* ferrous sulfate and mix. Finally, while holding the test tube at an angle of about 45°, *slowly* pour down the inside of the inclined test tube a volume of 18 *M* sulfuric acid approximately equal to the volume already in the test tube Do not mix. The formation of a brown ring at the interface of the two liquid layers indicates that nitrate ion was present in the unknown.

When the concentration of the nitrate ion is large enough, a brown band will form instead of the brown ring. Sometimes the action will be sufficient to spread the brown color throughout the solution. In such samples a brown ring can usually be obtained by considerable dilution of the starting solution.

(*d*) *Test for Sulfate Ion.* To the third portion of the filtrate from the sodium carbonate treatment add 6 *M* hydrochloric acid till the solution, after stirring, is acid to litmus. Add 5 cc. of 0.5 *M* barium chloride and then enough water to double the volume of the solution. If a white precipitate remains after the solution is well stirred, sulfate ion should be considered present.

Both chloride and sulfate ions are frequently found as impurities in laboratory reagents. Sometimes the distilled water dispensed in laboratories will give a faint chloride test. The water from the laboratory taps will often give either a chloride or sulfate test, or sometimes both. Ordinarily, "light" tests for chloride and sulfate ions indicate only the presence of these ions as impurities. Small amounts, or "traces" should be reported as such, or omitted from the report entirely.

64. Procedures for Carbonate, Sulfide, and Silicate Ions. (*a*) *Tests for Carbonate and Sulfide Ions.* Place a sample of the unknown of suitable size on a clean dry watch glass. Then add, drop by drop, 3 *M* sulfuric acid, best from a pipette rather than from the bottle. If the addition of acid causes effervescence (the formation of many small bubbles) carbonate or sulfide ions may generally be assumed present. Cautiously smell the gas

that escapes in the small bubbles. If it is odorless, or nearly so, carbonate ion should be considered present in the unknown, but if the foul odor of hydrogen sulfide is noted, sulfide ion may be considered present in the unknown. If both carbonate and sulfide ions were present in the same sample, the carbonate would be missed in this test.

Other substances beside carbonates and sulfides effervesce when placed in an acid solution. Finely divided metals will react to form hydrogen, which might be mistaken for the carbon dioxide from a carbonate. However, the action between a carbonate and acids is usually finished in a few seconds, while the reaction between a metal and an acid is usually slower. Sulfites and thiosulfates will effervesce in the presence of acids, but the gas given off is sulfur dioxide, the odor of which is not apt to be confused with that of hydrogen sulfide.

(*b*) *Test for Silicate Ion.* When an unknown sample requires a carbonate fusion to bring it into solution, and a white residue not dissolved by water or acids remains after the water soluble portion of the melt has been made acid, evaporated to dryness and baked, silicates probably are present in the unknown. If an unknown can be dissolved in water or acids without a carbonate fusion, silicates can be considered absent.

65. Significance of the Reaction of a Solution Toward Litmus. Solutions of acids or acid salts contain more hydrogen ion than hydroxide ion, turn litmus from blue to red, and are said to be acidic. Solutions of bases contain more hydroxide ion than hydrogen ion, and turn litmus from red to blue, and are said to be basic. However, solutions of many salts to which no acid or base has been added will change the color of litmus from blue to red or from red to blue. Solutions of some salts do not affect the color of litmus. So if a solution will change the color of litmus, the conclusion to be drawn is that that solution contains an excess of hydrogen or of hydroxide ion, according to the color change produced, but there is no warrant in concluding that either an acid or a base has been dissolved in the solution.

Reactions

66. Precipitation of the Metal Ions by Sodium Carbonate. The treatment of the unknown with sodium carbonate solution may produce any or all of the following effects. First, if there

was free acid in the solution, it is neutralized. For example, if the solution contained sulfuric acid, the reaction would be indicated by the equation

$$H_2SO_4 + Na_2CO_3 \rightarrow Na_2SO_4 + H_2O + CO_2\uparrow \qquad (82)$$

This reaction goes to completion in the direction indicated because carbon dioxide is a sparingly soluble gas which escapes as fast as it is formed, thus removing the possibility of a reverse reaction. Reactions usually go to completion when one of the products is a sparingly soluble gas. Thus, whenever acids react with sulfides, hydrogen sulfide gas escapes and the sulfide salt is dissolved.

A second effect produced by the addition of sodium carbonate solution, and in many instances the one chiefly sought, is the precipitation of nearly all of the metallic ions which may be present. The carbonates of nearly all the metals are sparingly soluble in water. The purpose of removing the metallic ions before testing for the negative ions is to keep the former from interfering with the tests. For example if an unknown should contain silver ion, a white precipitate of silver chloride would form when barium chloride was added in making the sulfate test. This could be mistaken for a true sulfate test.

However, the addition of sodium carbonate solution does not always completely precipitate all the metallic ions. For example, the ions of the alkali metals are not precipitated, nor are metals precipitated when they are present in negative ions such as AsO_4^{---}, CrO_4^{--} or MnO_4^{-}. It should be further noted that much of the sodium carbonate used as a laboratory reagent is prepared by the Solvay process and contains enough ammonia to form soluble complex ions with silver, copper, cadmium and other ions. The complex ions are not precipitated by the carbonate ion. Thoroughly boiling the solution lessens the effect thus produced.

A third effect produced by the sodium carbonate solution treatment is the partial dissolving of many substances that otherwise would require fusion.[1] Indeed, boiling with sodium carbonate solution can be viewed as a modified fusion. For example, if the unknown was silver chloride, its reaction with sodium carbonate solution can be represented by the equation

$$2\,AgCl + Na_2CO_3 \rightarrow Ag_2CO_3 + NaCl \qquad (83)$$

[1] See Chapter X.

The reaction proceeds only to a small extent toward the right, but after filtration the filtrate will usually contain enough sodium chloride to give a test for the chloride ion, while the undissolved silver chloride and the sparingly soluble silver carbonate will remain on the filter. In earlier times before the invention of the sodium carbonate fusion, repeated treatment with the sodium carbonate solution was used for dissolving refractory solids.

67. Chloride and Sulfate Ion Tests. The reactions used in the detection of chloride and sulfate ions have been met already in the analysis for the positive ions. When hydrochloric acid in sufficient concentration is mixed with barium chloride, white barium chloride is precipitated. This precipitate might easily be taken for a sulfate test. But if the volume of the solution is doubled by the addition of water, the concentration of the chloride ion is reduced so that the solid barium chloride passes into solution. Barium sulfate precipitate will not dissolve on the addition of the quantity of water indicated in the directions. It is to be noted that hydrochloric acid and barium chloride both contain chloride ion. Two substances having the same ion are said to have a *common ion.* When two substances having a common ion are placed in the same solution, and as a result one of them precipitates, the precipitation is said to be caused by the "common ion effect." The role of the common ion effect is discussed more fully in Chapter XII.

68. Nitrate Ion Test. The ring test for nitrates represents a somewhat complicated series of reactions. A full discussion of these reactions is omitted here. The brown ring probably results from the presence of oxides of nitrogen formed in the decomposition of nitrate ion accompanying the oxidation-reduction reaction between nitrate and ferrous ions.

QUESTIONS

1. What determines how much sample should be taken for analysis? If 10 cc. of a liquid unknown yielded a solid residue weighing 0.25 g. when evaporated to dryness, how many cubic centimeters of liquid should be taken to obtain a half gram of solute?

2. Why is it necessary to remove many metallic ions from a solution before making tests for the negative ions? Which positive ions are precipitated by sodium carbonate? Which metals might remain in a solution after the sodium carbonate treatment? Could a portion of the filtrate from the ammonium carbonate group be used to test for the negative ions? Which negative ions?

3. What chemical action would follow placing solid lead sulfate in a boiling solution of sodium carbonate?

4. Show where the reactions used in making the chloride and sulfate tests have been used previously.

5. In the test for the chloride ion why does the solution effervesce on the first addition of nitric acid but not after the second addition?

6. In the final test for chloride ion why does the addition of nitric acid cause silver *chloride* to precipitate?

CHAPTER X

THE ANALYSIS OF SOLID MATERIALS

Chapters IV to VIII inclusive describe methods that can be used for the detection of the more common positive ions when they are met in solutions. These same methods can be used for the analysis of solid inorganic materials if these solids are dissolved before beginning the analysis. If a solid unknown material can be dissolved by water or acids, getting the solid into solution is a simple matter. But some solids are met that are not affected by water or acid treatment. Getting such solids into solution is often as much of a task as is the analysis of the material after it is dissolved. The remainder of this chapter describes methods that may be used to dissolve solid unknowns before analyzing them by the methods in Chapters IV to VIII.

69. Preparation of the Sample. First examine the sample, noting the color and the odor, if there is any, and if possible note whether the material seems to be composed of one substance or more than one substance. Next finely powder about two grams of the solid. If the substance is a brittle metal it may often be powdered in the mortar. A tough metal may be powdered with a clean file, catching the filings on a piece of clean paper. In every case the sample of the unknown should be reduced to as small pieces as circumstances will allow, before any attempt is made to dissolve it.

Two general methods are described below for attempting to dissolve the solid material. The first and simpler of these is called the "Trial Method," while the second and more time-consuming is called the "Fusion Method." The more laborious fusion method will allow the dissolving of many solids not affected by the trial method. But the quickly applied trial method will be sufficient for dissolving most solids met in elementary courses in qualitative analysis and should always be tried before using the fusion method.

70. The Trial Method for Dissolving Solid Materials. The first step in this method is to try to dissolve a small portion of

the powdered unknown in water, as directed in the following paragraph. If this is unsuccessful, an attempt is made to dissolve a second small portion by means of some chemical reagent. If the first reagent tried does not work, other reagents are tried with other small portions till a reagent is found that will completely dissolve the trial portion. As soon as such a reagent is found, no further trials need be made. The reagent which dissolved the small trial portion is used to dissolve a sample of the unknown of a size suitable for analysis.

For the first trial, place in a test tube about one tenth gram of the finely powdered unknown and 5 cc. of water. Thoroughly agitate the contents of the tube. If solid matter remains, heat the liquid to boiling. Continue the agitation and boiling as long as any solid seems to be dissolving. If the trial sample (the one tenth gram portion) is dissolved by water, dissolve a 1 g. portion of the powdered sample (or, if the substance is a metal or alloy, use only 0.5 g.) in water and proceed with the separation and detection of the positive ions as directed in Chapters IV to VIII inclusive.

If the first trial sample was not dissolved by water, try in the same manner to dissolve other one tenth gram portions, one at a time, in 5 cc. portions of the following reagents, trying the reagents in the order given: 2 *M* hydrochloric acid, 2 *M* nitric acid, 6 *M* hydrochloric acid, 6 *M* nitric acid, 6 *M* sodium or potassium hydroxide, and a mixture of four volumes of 12 *M* hydrochloric acid with one volume of 16 *M* nitric acid.[1]

When a reagent is found that completely dissolves the trial portion, dissolve a 1 g. portion of the powdered unknown in as little of the reagent as possible. (Use a 0.5 g. portion if the unknown is a metal or an alloy.) When the sample is completely dissolved, start at the place indicated in the appropriate one of the following alternatives and analyze the solution for positive ions as directed in Chapters IV to VIII.

1. If the sample was dissolved by 2 *M* or 6 *M* hydrochloric acid, the hydrochloric acid group must be absent. Treat the solution as a filtrate from the hydrochloric acid group and begin with the precipitation of the hydrogen sulfide group, Section 23, page 34.

[1] Mixtures of hydrochloric and nitric acids are often called "aqua regia," latin for "king of liquids."

2. If the sample was dissolved by water or 2 *M* or 6 *M* nitric acid, begin with the precipitation of the hydrochloric acid group, Section 17, page 30.

3. If the sample was dissolved by 6 *M* sodium or potassium hydroxide, add 6 *M* hydrochloric acid to the solution containing the unknown till it is acid to litmus, then 10 cc. in excess. Shake well and start the analysis with the precipitation of the hydrogen sulfide group, Section 23, page 34.

4. If the sample was dissolved by the mixture of hydrochloric and nitric acids, aqua regia, evaporate the solution to a volume of about 2 to 3 cc., making use of a fume duct or a hood to avoid polluting the laboratory with the fumes. Add 50 cc. of water and continue the analysis beginning with the precipitation of the hydrogen sulfide group, Section 23, page 34.

The trial tests to see which reagent will dissolve the solid should not be hurried, as the process of dissolving is usually much slower than the reverse process of precipitation. Continued agitation and heating will often effect solution when a hasty treatment with the same reagent fails. If a trial portion is partly, but not completely, dissolved by one of the reagents other than water, or if the solution is clear when hot but a precipitate forms on cooling, try the effect of adding more water. If the addition of water causes more precipitate to form, try the effect of adding more acid. Whenever a choice of dissolving reagents is possible, the preference is in the following order: water, hydrochloric acid, nitric acid, sodium or potassium hydroxide, and aqua regia.

Sometimes a reagent will dissolve a solid completely except for a slight cloudiness or a few minute particles. Often no kind of ion will be lost if this solid material is removed by filtration and rejected. The slight cloudiness may be caused by impurities in the reagents. The solid particles may fail to be dissolved because the solid unknown was not sufficiently pulverized before beginning the analysis. Coarse particles dissolve more slowly than fine ones. Consult your instructor before rejecting any part of the unknown that does not dissolve.

71. The Fusion Method. This procedure uses water and acids to dissolve as much as possible of a 1 g. (0.5 g. if the unknown is a metal) sample of the finely powdered solid unknown. The solid residue unaffected by water and acids is filtered from the solution,

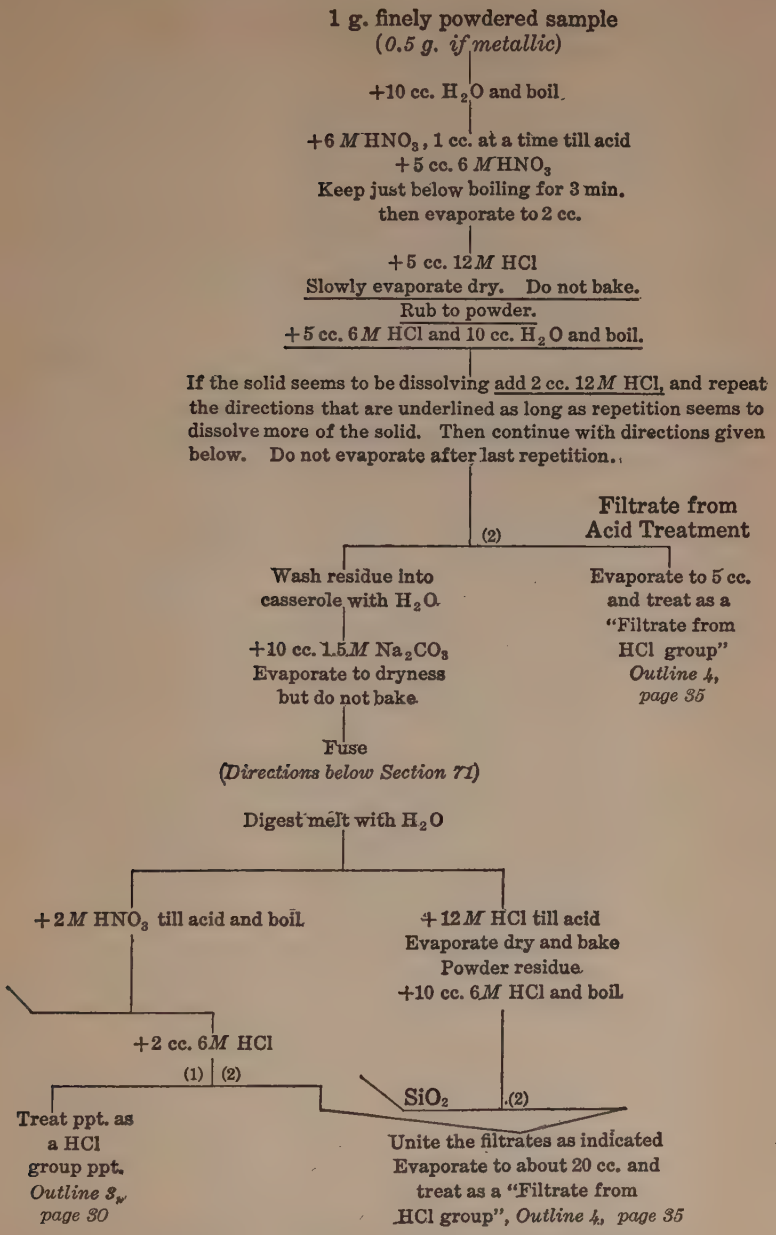
mixed with dry sodium carbonate and the mixture is melted or "fused," hence the name "fusion method." The details of the fusion method are given in Outline 12 and in the text in the following pages. Reference to the outline and the text show that there are two main parts in the fusion method, the acid treatment and the carbonate fusion. It will be further noted that the acid treatment is essentially a systematic arrangement of the trial method already described. In the carbonate fusion the sample undergoes a change such that after the fusion it can be dissolved by water and acids, which was not the case before the fusion. It may be mentioned that the carbonate fusion is useful not only for bringing refractory solids into solution, but, with certain limitations, it may be used to separate positive from negative ions in many mixtures.

Place 1 g. of the powdered unknown (0.5 g. if the unknown is a metal) in a beaker and treat it as directed in Outline 12. Other detailed directions are not given for the acid treatment, or for the procedure in general, but details as to the process of making a carbonate fusion are given in Section 72.

In using the procedure in the outline it may happen that the sample will be entirely dissolved before the end of the procedure is reached. Whenever the sample is entirely dissolved, all the subsequent directions in the outline as far as the words "*filtrate from acid treatment*" should be omitted. The analysis can be resumed after these words.

If the sample being analyzed requires fusion, time will ordinarily be saved if the fusion is made and the crucible and melt are placed in water before the analysis of the filtrate from the acid treatment is started.

72. Directions for Making a Carbonate Fusion. Obtain a 30 cc. nickel crucible, a bottomless clay crucible, and a Meker burner. Hereafter in this chapter "crucible" means a 30 cc. nickel crucible. If necessary, clean and dry the crucible by scouring with wet sand, washing with water, and gently heating. In a clean mortar place about 0.5 g. of dry potassium nitrate, about 10 g. of dry sodium carbonate and the solid residue from the acid treatment. Grind the mixture till it is thoroughly mixed and transfer the mixture to the clean crucible. Place a piece of paper under the crucible while the transfer is being made to catch any part that is spilled. This spilled part can also be


1 g. finely powdered sample
(0.5 g. if metallic)
+10 cc. H_2O and boil
+6 M HNO_3, 1 cc. at a time till acid
+5 cc. 6 M HNO_3
Keep just below boiling for 3 min.
then evaporate to 2 cc.
+5 cc. 12 M HCl
Slowly evaporate dry. Do not bake.
Rub to powder.
+5 cc. 6 M HCl and 10 cc. H_2O and boil.
If the solid seems to be dissolving add 2 cc. 12 M HCl, and repeat the directions that are underlined as long as repetition seems to dissolve more of the solid. Then continue with directions given below. Do not evaporate after last repetition.
(2)
Filtrate from Acid Treatment
Wash residue into casserole with H_2O
Evaporate to 5 cc. and treat as a "Filtrate from HCl group" Outline 4, page 35
+10 cc. 1.5 M Na_2CO_3
Evaporate to dryness but do not bake
Fuse
(Directions below Section 71)
Digest melt with H_2O
+2 M HNO_3 till acid and boil
+12 M HCl till acid
Evaporate dry and bake
Powder residue
+10 cc. 6 M HCl and boil
+2 cc. 6 M HCl
(1)
(2)
SiO_2
(2)
Treat ppt. as a HCl group ppt. Outline 3, page 30
Unite the filtrates as indicated
Evaporate to about 20 cc. and treat as a "Filtrate from HCl group", Outline 4, page 35

OUTLINE 12. The fusion method for dissolving solids. Acid treatment and carbonate fusion.

placed in the crucible. If the crucible is less than half full, add enough dry sodium carbonate to make it at least half full. The mixture in the crucible is now ready for fusion.

Place the crucible on a triangle on a ring stand. Over it, supported by the same triangle, place the bottomless clay crucible in an inverted position. Next apply the flame of the Meker burner to the bottom of the crucible till its contents are melted and small bubbles can no longer be seen in the melt. This should not require more than 15 to 20 minutes. If a longer time is required, something has been done wrongly, and the Instructor should be consulted.

To remove the melt, let the crucible cool and place it on its side in a beaker containing some water. The water should be deep enough to cover the crucible, but a minimum of water should be used. Let the melt soak till it loosens. This ordinarily requires from one to three hours. Letting it stand over night is a good plan. It is also a good plan to analyze the filtrate from the acid treatment for positive ions while the soaking is in progress. When the melt has loosened so that it feels soft and crumbly when prodded with a stirring rod, remove the crucible with a stirring rod. Wash its exterior with a stream from the wash bottle before touching it with the fingers. Transfer any solid remaining in the crucible to the casserole with the help of a stirring rod or a stream of water from the wash bottle. If any lumps are noticed in the casserole break them to small pieces with a blunt stirring rod or a pestle. Finally boil the solution for a few moments to aid the dissolving of the soluble part of the melt. Resume the analysis at that point on Outline 12 following the words "*Digest melt with water.*"

The melt can be removed from the crucible in less time, but with more work than the above directions require, if as much as possible of the melt, while still molten, is poured from the crucible into the water in the beaker. Then submerge the hot crucible also in the beaker. Finally, gently boil the solution in the beaker until the melt loosens.

Reactions Involved in Dissolving Solids

73. Dissolving Solids by Means of Acids. When a solid which is not soluble in water is dissolved by treatment with an acid solution, a reaction takes place which in most cases is a double

decomposition, though in some cases it is an oxidation-reduction reaction. Many such reactions have been met already. For example, in the beginning of the analysis of the ammonium carbonate group precipitate, page 71, calcium carbonate is dissolved by hydrochloric acid.

$$CaCO_3 + 2\ HCl \rightarrow CaCl_2 + H_2O + CO_2\uparrow \quad (84)$$

$$CO_3^{--} + 2\ H^+ \rightarrow H_2O + CO_2\uparrow \quad (85)$$

In the beginning of the copper group analysis, page 38, copper sulfide is dissolved by nitric acid.

$$3\ CuS + 8\ HNO_3 \rightarrow 3\ Cu(NO_3)_2 + 4\ H_2O + 2\ NO\uparrow + 3\ S\downarrow \quad (86)$$

Thus, while calcium carbonate and copper sulfide are soluble to only a slight extent in water, they are dissolved by the acid solutions because they react with the acids to form calcium chloride and copper nitrate, respectively, which are soluble in water. It is not correct to say that calcium carbonate is soluble in hydrochloric acid. Calcium carbonate is only slightly more soluble in hydrochloric acid than in water, but owing to the reaction by which the very soluble calcium chloride is formed, much calcium carbonate can be *dissolved by* a hydrochloric acid solution.

74. Dissolving Solids by Means of Sodium or Potassium Hydroxide. Many substances which are not dissolved by acids can be dissolved by solutions of strong bases. Such substances are frequently oxides or other compounds of elements which can enter the composition of a negative ion. For example arsenic oxide is dissolved by sodium hydroxide solution, although it is not easily completely dissolved by either water or acids.

$$As_2O_3 + 6\ NaOH \rightarrow 2\ Na_3AsO_3 + 3\ H_2O \quad (87)$$

When sodium arsenite ionizes, the negative ion is AsO_3^{---}. The elements lead, arsenic, antimony, tin, zinc, and aluminum are often found in negative ions. As a general, though not universal, rule the higher the valence of a metallic constituent of a compound the greater will be its tendency to become part of a negative ion.

75. The Solubility of Various Substances. In connection with the dissolving of solids it may be helpful to mention what classes of substances are generally soluble in water, what classes are

dissolved by treatment with acids, and what classes require fusion. In reading the following generalized statements it should be remembered that a generalized statement is usually, but not always, true. The term soluble, as here used, implies solubility to a degree useful in dissolving unknowns preparatory to analysis.

1. Substances soluble in water:[1]
   a. All nitrates.
   b. All salts of the alkali group metals.
   c. All chlorides except lead, silver and mercurous chlorides.
   d. All sulfates except lead, silver, mercurous, barium, and calcium sulfates.
2. Substances not soluble in water.
   a. All metallic oxides and hydroxides except those of barium, calcium and the alkali metals.
   b. All metallic sulfides.
   c. All carbonates except those of potassium, sodium and ammonium.
3. Substances dissolved by dilute acids.
   a. Most oxides and hydroxides.
   b. All sulfides and carbonates.
   c. Other salts of weak acids.
4. Substances requiring fusion.
   a. Oxides and salts not dissolved by acids.
   b. Slightly soluble salts of strong acids.

76. Carbonate Fusion. The carbonate fusion is effective in dissolving almost any substance that is not volatilized below about 1000°. Its use in the laboratory is probably most often required for dissolving substances containing silicon compounds. Many of these have been exposed to high temperatures, hence are sometimes termed "igneous" substances. Examples of igneous substances are blast furnace slags, smelter mattes, glass, cement, porcelain, china ware, bricks and tiles as well as nearly all soils, clays and rocks.

As examples of non-igneous substances often requiring fusion before they can be dissolved may be mentioned silver chloride,

[1] The salts of bismuth, antimony, and tin, when placed in water react with the water to form white precipitates; in other words they hydrolyze. If dissolved in an acid solution of sufficient concentration, clear solutions result, but if the concentration of the acid in such a solution is sufficiently lessened, either by dilution with water or by the addition of a base, white precipitates will again appear even though the solution is still acid toward litmus.

mercurous chloride, antimony and tin oxides, lead sulfate, and barium sulfate.

The carbonate fusion represents a different type of reaction from most of those met in qualitative analysis, a reaction not in water solution, but in molten sodium carbonate solution. To afford an idea of what happens during the process of fusion, the reactions used in dissolving the familiar refractory substance asbestos (magnesium calcium silicate) will be described. The reaction during fusion may be represented by the following equation.

$$\underset{\substack{\text{Insol. in water.}\\ \text{Not dissolved}\\ \text{by acids.}}}{Mg_3Ca(SiO_3)_4} + 4\ Na_2CO_3 \rightarrow \underbrace{3\ MgCO_3 + CaCO_3}_{\substack{\text{Insol. in water.}\\ \text{Dissolved by acids.}}} + \underset{\text{Sol. in water.}}{4\ Na_2SiO_3} \quad (88)$$

When the melt is treated with water, the part that dissolves is called the "soluble portion" and the part that does not dissolve, the "insoluble portion." Here the soluble portion will contain sodium silicate and also the excess sodium carbonate and the potassium nitrate, while the insoluble portion will be composed of a mixture of calcium and magnesium carbonates. After fusion the metallic elements of the asbestos are found in the insoluble portion and the acid radical is found in the soluble portion. Thus it is seen that fusion, besides providing a method for dissolving refractory materials, provides also a method for separating the positive from the negative ions in an unknown. At this point it may be well to recall that many negative ions contain a metallic constituent, and that if substances containing such ions are fused, these metallic constituents will be found in the soluble portion. Arsenate, antimonate, chromate, and permanganate ions are examples. For this reason the soluble portion is also analyzed for metallic ions.

After the soluble and insoluble portions of the melt have been digested in water and separated by filtration, each receives a different treatment, after which they are united for further analysis as indicated in the outline. In the rather simple treatment given to the insoluble portion, it is dissolved by 2 *M* nitric acid and any ions of the hydrochloric acid group are removed before union with the solution finally obtained from the soluble portion. In the treatment given to the soluble portion the solution is made acid with 12 *M* hydrochloric acid.

$$Na_2CO_3 + 2\ HCl \rightarrow H_2O + CO_2\uparrow + 2\ NaCl \qquad (89)$$

$$Na_2SiO_3 + 2\ HCl \rightleftarrows H_2SiO_3 + 2\ NaCl \qquad (90)$$

Note that in Equation 90 both of the products are soluble and that the reaction is reversible. The process of evaporating to dryness and baking the residue affects only the silicic acid.

$$H_2SiO_3 \rightarrow H_2O\uparrow + SiO_2 \qquad (91)$$

As the silicon dioxide (sand) is not soluble in water, the reaction is not reversible. This procedure is often spoken of as "dehydrating the silica." Since the presence of soluble silicate ions interferes with many reactions in the scheme of analysis it is important that it be removed. The "dehydration of the silica" provides a rather simple method for its removal.

After baking, the residue is treated with 6 *M* hydrochloric acid to help dissolve any substance mixed with the sand. If the sand has not a pure white color after the first acid treatment, the treatment should be repeated till the color is white. This hydrochloric acid wash is not united with the solution of the insoluble portion of the melt till the hydrochloric acid group has been removed from the latter, because of possible interference by chloride or sulfate ions that might be present in the hydrochloric acid wash from the dehydrated silica.

The role of the small quantity of potassium nitrate used in the fusion mixture is that of an oxidizing agent. As a general rule (not always) the higher the valence of a positive ion the more soluble are its compounds. Hence, oxidation usually increases solubility. An oxidizing agent will also tend to destroy small quantities of organic matter (carbon compounds) if any was present in the sample. If more than a small quantity of potassium nitrate is used, the mixture may be harder to fuse than otherwise.

Since a carbonate fusion is rather easily made, and since by it practically everything can be dissolved, the question may arise "Why not make a fusion in the first place and omit the work of the acid treatment?" A temperature of from 800 to 900° is necessary to cause fusion. Any compounds that vaporize at or below these temperatures would be lost if they were not removed before the fusion. Nearly all compounds of mercury, arsenic, antimony and ammonium would thus be vaporized. By the acid

treatment such volatile compounds are removed from the sample before it is fused.

The process of fusion usually dissolves enough of the crucible to give a test for the metal or metals of which it is composed. If this metal was found in the analysis of the fused portion there would be no means of telling whether it was in the sample before fusion or not. Similar reasoning applies to the sodium and potassium ions introduced as fluxing materials. (A flux is a substance mixed with another substance to promote fusion.)

On account of the foregoing considerations the procedure is planned so that the solution resulting from the acid treatment is analyzed by itself, and the solution resulting from the fusion is analyzed by itself.

QUESTIONS

1. Name three positive ions that form few salts that are not freely soluble in water; three negative ions.

2. What four classes of compounds are generally only slightly soluble in water?

3. What two negative ions form salts only slightly soluble in water, but dissolved by most dilute acids?

4. The presence of what salt might be indicated if an unknown was completely dissolved by hot water but a precipitate formed on cooling? (See Chapter IV.)

5. What should be done when the trial method found successful in dissolving the 0.1 g. trial sample, seemingly fails to dissolve the 1 g. sample?

6. What inference concerning the composition of the unknown may be drawn if the solid material is completely dissolved by hydrochloric acid but a white precipitate forms when the solution is diluted with water? What should be done in such a case?

7. What desirable, as well as undesirable results might be expected if a 5 g. instead of a 1 g. sample was used for the positive ion analysis? If a 0.25 g. sample was used?

8. If the unknown was dissolved by aqua regia, predict the effects on the course of the analysis that might follow if the solution was not evaporated to a small volume (the directions specify 2 to 3 cc.) before beginning the positive ion analysis.

9. If a carbonate fusion is necessary to dissolve an unknown, why not omit the acid treatment and fuse a portion of the original unknown?

10. Write equations for the reactions involved in getting silver chloride into solution by using the carbonate fusion. Do the same for lead sulfate. How can the carbonate fusion be used to separate a positive from a negative ion in a salt?

11. Compute the weight of sodium carbonate that would react with 1 g. of asbestos. Why is so great an excess used in the fusion mixture? What finally becomes of the unused excess?

12. Name some negative ions which contain a metallic constituent.

13. Why might the use of hydrochloric or sulfuric acid be objectionable for dissolving the insoluble portion of the melt?

14. Consider the residue obtained when the soluble portion of the melt is made acid, evaporated to dryness and baked; what conclusion might be drawn if this residue was entirely dissolved by the 6 *M* hydrochloric acid added?

CHAPTER XI

THE MOLE AS A UNIT OF MEASUREMENT

The quantity of a solid substance is conveniently measured by its weight. Weight may be expressed in grams, pounds, tons or other units. Numbers of objects may be expressed in dozens, scores, gross, or millions. In all cases utility is the guide employed in selecting either a unit of weight or of number. In chemical work where both the weights of substances and the numbers of molecules of substances entering a chemical reaction are of importance, a single unit of measurement is used which expresses both weight and number of molecules. It is the gram-molecular weight, more commonly abbreviated to the term "mole."

77. The Mole. A mole of any pure substance is 606,000,000,000,000,000,000,000 (6.06×10^{23}) molecules of that substance. This very large number is called Avogadro's number and is frequently denoted by the letter N. (Do not confuse the use of the letter N to denote Avogadro's number with the occasional use of the same letter N to stand for the word "normal" in expressing the concentration of a solution.) While the number of molecules in a mole of any substance is always the same, the weight in grams of one mole of different substances varies widely. An analogy may illustrate this point. The number of pieces in a dozen eggs is equal to the number of pieces in a dozen bricks, but the weight in grams of a dozen eggs and of a dozen bricks will be quite different. In the case of eggs and bricks there is only one direct method of learning the weight of a dozen pieces of either, that is to weigh them. But the weight in grams of N molecules (one mole) of any pure substance is always numerically equal to the molecular weight of that substance. Thus N molecules (one mole) of water (mol. wt. 18) weigh 18 grams, while N molecules (one mole) of hydrochloric acid (mol. wt. 36.45) weigh 36.45 grams. Hence one molecule of hydrochloric acid is about twice as heavy as one of water. Also, if one mole (N molecules) of water weighs 18 grams, the weight of one molecule of water is obtained by dividing 18 by N.

78. Molar Concentration. The mole is frequently used to express the concentration of solutions. The concentration of a solution may be expressed by stating the quantity of solute per liter of solution. Thus if eight ounces of sugar was dissolved in enough water to make a liter of solution, the quantity of sugar per liter of solution would be eight ounces and the concentration 8 ounces per liter. Obviously other units than ounces and liters could be used in expressing concentration. Molar concentration is the number of moles of solute per liter of solution. The molecular weight of cane sugar is 342, hence one mole of sugar will weigh 342 grams, and a one molar sugar solution will contain 342 grams of sugar per liter of solution.

So long as chemical thinking concerns itself with the *weights* of substances taking part in a chemical reaction the measurement of concentration in moles per liter offers no advantage over grams per liter. But when chemical thinking concerns itself with the *numbers of molecules* or other unit pieces of matter taking part in a chemical reaction, the usefulness of the mole as a unit of measurement becomes apparent. For example the molecular weight of alcohol is 46 and that of sugar is 342. Hence a liter of 1 molar alcohol solution contains 46 grams of alcohol while a liter of 1 molar sugar solution contains 342 grams of sugar, more than seven times as much by weight, yet equal volumes of these solutions contain the same number of molecules. The two solutions will have the same freezing point, because the freezing point depends on the numbers of dissolved molecules per unit volume of solution. Similarly certain other properties of the two solutions will be the same.

Thus far it has been tacitly assumed that when a solid is dissolved in water it becomes separated into a very large number of very small pieces called molecules and that the composition of each molecule is correctly represented by the formula of the solid. Thus cane sugar has the formula $C_{12}H_{22}O_{11}$ and the presumption is that each of the molecules of sugar in a sugar solution is composed of 12 carbon atoms, 22 hydrogen atoms and 11 oxygen atoms. This presumption that the formulas of substances correctly represent the composition of the dissolved molecules of solute existing in a solution is in harmony with the experimental facts so long as the substances considered are non-electrolytes like sugar or alcohol. But most substances met

in qualitative analysis are electrolytes, that is acids, bases, or salts. The question may well be raised in considering a solution in which silver chloride or barium sulfate is dissolved as to whether or not composition of the dissolved molecules is correctly represented by the formula AgCl or $BaSO_4$. Many experimental facts are more reasonably explained if the assumption is made that such sparingly soluble substances when dissolved are entirely dissociated into ions. Thus, it may be assumed that there are no silver chloride molecules in solution, only Ag^+ ion and Cl^- ion; that there are no barium sulfate molecules in solution, only Ba^{++} ion and SO_4^{--} ion. If this theory is true, the expression "molecules of silver chloride" is only a convenience of language to denote equal numbers of silver ions and chloride ions. This is also true of barium sulfate and other salts. From this viewpoint the statement that the concentration of a certain silver chloride solution was 1.5×10^{-7} molar would imply that in this solution there were 1.5×10^{-7} moles of silver ion and 1.5×10^{-7} moles of chloride ion.

79. Molar Solubility. The concentrations of saturated solutions are of particular importance in qualitative analysis because before a precipitate can begin to form, the solution must be saturated with respect to the substance of which the precipitate is composed. The concentration of a saturated solution of any substance is said to be the "solubility" of that substance. Here again convenience in use is the guide in choosing units for expressing concentration, or solubility. For many purposes solubility is best expressed in moles of solute per liter of solution. A liter of a saturated solution of sodium chloride (Mol. Wt. 58.46) contains 357 grams of solute. The molar solubility of sodium chloride is found by calculating the number of moles in 357 grams of this substance. When 357 is divided by 58.46 the number 6.1 is obtained as the number of moles in one liter of a saturated solution of sodium chloride. Since what is commonly called a sodium chloride molecule is really one sodium ion and one chloride ion, it follows that a saturated sodium chloride solution must contain 6.1 times N sodium ions and 6.1 times N chloride ions per liter, and its molar solubility is said to be 6.1 *M*.

The following problems should be worked for purpose of review and as an exercise in the use of the ideas presented above. Students who meet difficulty in the multiplication and division

of the very large and very small numbers met in some of the following problems are referred to the section entitled "A Lesson in Exponential Arithmetic" placed at the close of this chapter.

PROBLEMS

1. How many grams are there in 1 mole of Cl_2, HCl, NaCl, NaOH, $FeSO_4$, H_2SO_4, $AlCl_3$, $Cu(NH_3)_4SO_4$?

2. Compute how many grams of each of the substances in Question 1 will be needed to make 1 liter of 1 *M* solution? In each case how many grams will there be in 100 cc. of a 1 *M* solution? In 1 cc.? In 250 cc.?

3. How many cc. of 1 *M* HCl will react with one mole of each of the following: NaOH, $Ca(OH)_2$, $Al(OH)_3$? How many cc. of 1 *M* H_2SO_4 will react with one mole of each of these substances?

4. How many moles of solute are there in the indicated quantities of each of the following solutions: 500 cc. of 5 *M* H_2SO_4, 6 cc. of 2 *M* $AlCl_3$, 15 cc. of 0.0003 *M* $AgNO_3$?

5. Assuming that the volumes of mixed solutions are perfectly additive, compute the molar concentration that would result from mixing a liter of water and a liter of 2 *M* H_2SO_4? 1 liter of water and 500 cc. of 1 *M* HCl? How many cc. of water must be mixed with 20 cc. of 3 *M* H_2SO_4 to get a 2 *M* H_2SO_4 solution?

6. Compute the molar concentration of a nitric acid (Mol. Wt. 63) solution containing 378 grams of solute per liter of solution.

7. Compute the molar concentration of a nitric acid (Mol. Wt. 63) solution containing .0043 grams of solute in 15 cc. of solution.

8. How many hydrogen atoms are there in 1 molecule of H_2SO_4? How many sulfur atoms? How many oxygen atoms?

9. How many sulfuric acid molecules are there in 1 mole of that substance? How many hydrogen atoms are there in 1 mole of H_2SO_4? How many sulfur atoms? How many oxygen atoms?

10. If 1 mole of sulfuric acid weighs 98 grams, what is the weight of 1 molecule of H_2SO_4? Is this more or less than the weight of 1 molecule of Na_2CO_3?

11. Which contains more molecules, 1 pound of salt (Mol. Wt. 58.5) or 1 pound of sugar (Mol. Wt. 342)?

12. If 1 cc. of water weighs 1 gram, compute the number of moles, also the number of molecules, in 1 cc. of water. What is the greatest volume 1 molecule of water could occupy? (By knowing the volume occupied by 1 molecule of substance some idea of its diameter is obtained.)

13. What is the molar solubility of potassium chloride (Mol. Wt. 74.6) if a liter of saturated solution contains 285 grams of solute?

14. What is the molar solubility of mercurous chloride (Mol. Wt. 236) if a liter of saturated solution contains 0.00000045 (4.5×10^{-7}) grams of solute?

15. If the molar solubility of potassium chlorate is 0.52, compute the number of grams in 100 cc. of saturated solution. In 475 cc. In 0.00039 cc.

16. Which is more soluble, barium oxalate the molar solubility of which is 3.8×10^{-4} or calcium oxalate the molar solubility of which is 4.3×10^{-5}?

17. The molar solubilities of both silver chloride and barium sulfate have nearly the same value, 1.0×10^{-5}. Which will contain more molecules of the solute, one liter of saturated silver chloride solution or 1 liter of a solution saturated with barium sulfate? Which will contain more grams of solute per liter of solution? How much more? Which solution is more concentrated?

18. If the molar solubility of lead sulfate is 1.3×10^{-4}, what is the molar concentration of the lead ion and of the sulfate ion?

19. If the molar solubility of barium chromate is 1.5×10^{-5}, are there more barium ions or chromate ions in 1 liter of saturated solution? Are there more grams of barium ions, or of chromate ions?

20. The solubility of mercuric sulfide is 4.7×10^{-25} grams per liter. Compute the molar solubility of mercuric sulfide. Compute the molar concentration of the mercuric ion. Of the sulfide ion. How many mercury ions are there in each cc. of the solution?

A Lesson in Exponential Arithmetic

Labor is often saved by using exponential arithmetic for expressing very large and very small numbers. In this method the very large or very small number is written as a product of two numbers. The first member of this product, called the *digit* term, is usually written as a number not less than 1 or more than 10. The second member of the product, called the *exponential* term, is expressed by a 10 with an exponent. The following examples illustrate both the common and exponential methods of expressing numbers greater than 10.

Common Method	Exponential Method
10	1.0×10^{1}
25	2.5×10^{1}
257	2.57×10^{2}
2500	2.5×10^{3}
2549	2.549×10^{3}

In the above examples it should be noted that in every case the exponent of 10 is numerically equal to the number of places the decimal was shifted in obtaining the digit term from the number expressed by the common method. Thus, in the last example given above, 10 has an exponent 3, and to change from 2549 to 2.549 the decimal point was shifted three places. This principle serves as a guide in transposing numbers from one system to the other.

Students should work all the examples given in this section to familiarize themselves with the meaning conveyed in the text. Answers will be found at the end of the chapter.

1. Express exponentially 37; 459; 4976; 85700; 670,000,000,000; 606,000,000,000,000,000,000,000.

2. Change the following to common numbers: 3.75×10^{2}, 4.96×10^{12}, 4.586×10^{2}, 9.876×10^{7}.

In using exponential numbers to express the experimental data introduced in the later chapters, the accuracy of the data seldom requires more than two figures after the decimal point of the digit term. In many cases the accuracy of the data does not warrant more than one figure after the decimal

in the digit term. Hence in the remainder of this "lesson in arithmetic" the digit term seldom carries more than one figure after the decimal. Similar accuracy is sufficient in working the problems given.

Numbers between 1 and 10 can be written exponentially by setting down the digit term by the method already shown and by writing the 10 in the exponential term as having an exponent of zero. Thus 2.5 becomes 2.5×10^0, 9.875 becomes 9.875×10^0, while 1 itself becomes 1.0×10^0. That is, 10^0 equals 1. The meaning of ten to the zero power (10^0) may be intangible to students who have never had algebra. The matter is here stated as a fact without attempt at proof.

After presenting exponential numbers such as 3.7×10^{12} where the exponent is positive and numbers such as 2.5×10^0 where the exponent is zero, a next question in many minds would be "What is the meaning of expressions such as 3.4×10^{-5} where the exponent has a negative value?" The answer to this question is more easily understood after some problems in multiplication and division of exponential numbers have been worked.

The following example illustrates the method of finding the product of two exponential numbers (multiplying).

Problem: multiply 1.5×10^{14} by 6.0×10^{12}. Write the problem like this

$$\begin{array}{r} 1.5 \times 10^{14} \\ 6.0 \times 10^{12} \\ \hline \end{array}$$

Then underneath the digit terms set the product of the digit terms and underneath the exponential terms set the product of the exponential terms, thus

$$\begin{array}{r} 1.5 \times 10^{14} \\ 6.0 \times 10^{12} \\ \hline 9.0 \times 10^{26} \end{array}$$

From the foregoing it will be seen that the product of the digit terms (1.5 times 6.0) is obtained by ordinary arithmetic, while the product of the exponential terms ($10^{14} \times 10^{12}$) is obtained by adding the exponents. That is, $10^{14} \times 10^{12} = 10^{14+12} = 10^{26}$. The *addition* of exponents to multiply the exponential terms is a fact that students of limited mathematical training should remember.

3. Multiply 1.5×10^{12} by 1.5×10^{21}; 2.75×10^{17} by 3.56×10^{49}.

The process of division of exponential numbers, as illustrated in the following example, is quite suggestive of the process of cancellation.

Problem: divide 3.6×10^8 by 1.8×10^5. Set the problem down as in cancellation, thus,

$$\frac{3.6 \times 10^8}{1.8 \times 10^5}$$

To solve this problem divide the expression below the line into the expression above the line, the digit term into the digit term as in ordinary arithmetic, and the exponential term into the exponential term by subtracting the exponent below the line from the exponent above the line. Thus,

$$\frac{2.0 \quad 10^3}{\cancel{3.6} \times \cancel{10^8}} = 2.0 \times 10^3 \text{ Answer.}$$
$$\cancel{1.8} \times \cancel{10^5}$$

In the above example by dividing 3.6 by 1.8 the quotient 2 is obtained as the digit term of the answer, while to divide 10^8 by 10^5 in the division of the exponential terms we simply subtract 5, the exponent below the line, from 8, the exponent above the line, and obtain 10^3 as the exponential part of the answer. To the non-mathematical student the important thing to remember is that one ten with an exponent may be divided by another ten with an exponent by *subtracting* the second exponent from the first exponent. In the above problem $10^8 \div 10^5 = 10^{8-5} = 10^3$. The methods for multiplication and division just given can be verified by working the same or similar problems by ordinary arithmetic.

4. Divide 3.4×10^6 by 1.7×10^4; 1.75×10^{40} by 1.25×10^{15}; 3.6×10^2 by 1.8×10^4.

In trying to solve the last part of Problem 4 one is called upon to divide 10^2 by 10^4. This gives 10^{2-4}, that is, the exponent of the resulting quotient is two less than zero. Such numbers, called negative numbers, are often met. The question of the meaning of these negative exponents will now be answered. A negative exponent was met when 3.6×10^2 was divided by 1.8×10^4 exponentially and working the same problem by ordinary arithmetic will lead to a correct interpretation. Thus

$$\frac{3.6 \times 10^2}{1.8 \times 10^4} = \frac{360}{18000} = \frac{2}{100} = 0.02 = \frac{2}{0^21} = 2 \times 10^{-2}$$

That is, an exponential number in which the exponent is negative is equal to a common fraction in which the digit term is the numerator and the exponential term with the negative sign omitted is the denominator, or it is equal to a decimal fraction which can be obtained from the exponential number by entirely dropping the exponential term and by moving the decimal point of the digit term to the left a number of places numerically equal to the negative exponent. The transposition to decimal fractions is the one most often needed in this book. The foregoing paragraph is more briefly and less exactly stated in the sentence, "Exponential numbers containing negative exponents represent fractions."

The practical application of the relation between decimal fractions and exponential numbers is illustrated in the following examples.

$$4.5 \times 10^{-1} = 0.45$$
$$4.5 \times 10^{-2} = .045$$
$$4.5 \times 10^{-3} = .0045$$
$$4.5 \times 10^{-9} = .000,000,004,5$$

5. Write the following exponential numbers as decimal fractions: 1.0×10^{-1}, 3.56×10^{-3}, 7.8946×10^{-8}.

6. Express the following decimal fractions as exponential numbers: 0.9, 0.975, 0.032, 0.0000458735, 0.000,000,000,084,3.

From the examples just given it can be seen that the decimal point of the digit part of a number can be shifted any number of places, either to the left or to the right, without changing the value of the expression, provided a corresponding change is made in the value of the exponent of 10 in the exponential term of the same number. The following expressions all have the same value, namely one, or unity.

$$\begin{aligned} 100.0 &\times 10^{-2} \\ 10.0 &\times 10^{-1} \\ 1.0 &\times 10^{0} \\ 0.1 &\times 10^{1} \\ 0.01 &\times 10^{2} \\ 0.001 &\times 10^{3} \end{aligned}$$

Of course writing numbers this way violates the rule by which the digit term was given a value between 1 and 10. In actual work it is sometimes convenient to violate the rule in this way.

The method for multiplying and dividing exponential numbers having negative exponents is the same as that used for those having positive exponents. However the negative exponents must be added or subtracted "algebraically."

Examples:

$$(4.8 \times 10^{-4}) \times (1.0 \times 10^{-7}) = 4.8 \times 10^{-11}.$$
$$(4.8 \times 10^{-4}) \times (1.0 \times 10^{7}) = 4.8 \times 10^{3}.$$
$$(4.8 \times 10^{4}) \times (1.0 \times 10^{-5}) = 4.8 \times 10^{-1}.$$

7. Multiply 1.2×10^{-4} by 6.0×10^{-5}; 4.8×10^{0} by 1.7×10^{-3}; 9.7×10^{-16} by 1×10^{150}.

Examples of division:

$$3.6 \times 10^{7} \text{ divided by } 1.8 \times 10^{5} = 2.0 \times 10^{2}$$
$$3.6 \times 10^{7} \text{ divided by } 1.8 \times 10^{-5} = 2.0 \times 10^{12}$$
$$3.6 \times 10^{-7} \text{ divided by } 1.8 \times 10^{-5} = 2.0 \times 10^{-2}$$

8. Divide 4.8×10^{-17} by 2.0×10^{-14}; 3.6×10^{12} by 2.4×10^{-25}; 9.8×10^{-14} by 3.7×10^{-45}; 4.8×10^{16} by 6.5×10^{-12}.

9. Which number is larger, 9.0×10^{-21} or 3.0×10^{-14}? How many times as large?

ANSWERS TO PROBLEMS

1. 3.7×10^{-1}; 4.59×10^{2}; 4.976×10^{3}; 8.57×10^{4}; 6.7×10^{11}; 6.06×10^{23}.
2. 375; 4,960,000,000,000; 458.6.
3. 2.25×10^{33}; 9.8×10^{66}.
4. 2.0×10^{2}; 1.4×10^{25}; 2.0×10^{-2}.
5. 0.1; 0.00356; 0.000,000,078,946.
6. 9.0×10^{-1}; 3.2×10^{-2}; 4.6×10^{-5}; 8.43×10^{-11}.
7. 7.2×10^{-9}; 8.8×10^{-3}; 9.7×10^{134}.
8. 2.0×10^{-3}; 1.5×10^{37}; 2.6×10^{31}; 0.74×10^{28} which equals 7.4×10^{27}.
9. 3.0×10^{-14} is larger. 0.33×10^{7}, or 3,300,000 times as large.

CHAPTER XII

PRECIPITATION

The formation and the dissolving of precipitates are met so often in qualitative analysis that a study of these processes is desirable. It may be stated as an experimental fact that before a precipitate can begin to form in a solution, the solution must be saturated with respect to the salt composing the precipitate. Precipitation and filtration never completely remove a substance from solution. If a salt has been precipitated from a solution and the precipitate has been removed by filtration, the filtrate will still be saturated with the salt composing the solid precipitate. Of course the less soluble the precipitate, the less of it will remain in the solution after filtration.

Another experimental fact is that when a solid salt is placed in an unsaturated solution of that salt, the solid will dissolve till the solution becomes saturated or till none of the solid remains. This latter statement gives an idea of the conditions that must be met before a precipitate or a solid substance can be dissolved. In the following sections of this chapter are given more detailed statements of the conditions that exist when precipitates are formed or dissolved.

80. The Solubility Product Law. (*a*) *Simple Statement.* In the sciences a law is usually a generalized statement of how natural objects have been observed to exist or behave, or of how natural phenomena have been observed to take place. That is, laws are summarized statements of the results of many observations or experiments. The solubility product law is such a statement concerning the concentrations of the ions in saturated solutions of electrolytes. A statement of this law is that in a saturated solution of a slightly soluble electrolyte the product of the molar concentrations of the ions is equal to a fixed number, called the solubility product (or ion product constant) characteristic of the particular electrolyte. This number usually varies when the temperature varies and is different for different substances, but is always the same for a given substance at a given

temperature. This is true, with certain limitations, regardless of what other substances are present in the solution.

(*b*) *Illustration.* As an illustration of the solubility product law it may be stated that in a water solution saturated with lead sulfate at about 25° C. and containing no other dissolved substances the concentration of the lead ion is 1.5×10^{-4} (or 0.00015) moles per liter and that of the sulfate ion is the same. Hence, for lead sulfate the product of the molar concentrations of the ions is (1.5×10^{-4}) times (1.5×10^{-4}) which is 2.3×10^{-8}. This is more commonly written

$$C_{Pb^{++}} \times C_{SO_4^{--}} = (1.5 \times 10^{-4}) \times (1.5 \times 10^{-4}) = 2.3 \times 10^{-8}.$$

The number 2.3×10^{-8} is the solubility product or ion product constant of lead sulfate.

It has been assumed that lead sulfate was the only dissolved substance present in the saturated solution. That is why the concentration of the lead ion and the sulfate ion were considered equal. However, it would be possible to saturate a sulfuric acid solution with lead sulfate. In such a solution the number of sulfate ions would be greater than the number of lead ions, but the product of the molar concentrations of the two ions would still be 2.3×10^{-8}. There is no distinction between a sulfate ion that came from sulfuric acid and one that came from lead sulfate. It is the total sulfate ion concentration with which the solubility product law is concerned. On the other hand, if the temperature of the saturated solution is changed, the molar concentrations of the lead and sulfate ions are changed in such a way that the product of the molar concentrations would no longer be equal to 2.3×10^{-8}.

(*c*) *More General Statement of the Law.* In the manner in which it is stated above, the law applies only to electrolytes like silver chloride or lead sulfate which give equal numbers of positive and negative ions when dissolved in water. For substances such as lead chloride, $PbCl_2$, and antimony sulfide, Sb_2S_3, which form unequal numbers of positive and negative ions when dissolved in water, a slightly amplified statement of the law is necessary. This more general statement is most simply made in mathematical terms. If the formula A_mB_n represents any slightly soluble electrolyte (such as silver chloride, lead chloride or antimony sulfide) where A and B represent the

chemical symbols, respectively, of the positive and negative ions, and m and n represent the numbers of atoms of A and B per molecule, then the solubility product of A_mB_n is

$$(C_A)^m \times (C_B)^n = K \text{ (solubility product)}.$$

The solubility product of antimony sulfide for example is

$$(C_{Sb^{+++}})^2 \times (C_{S^{--}})^3 = K.$$

The solubility product law as stated is only an approximation. It approaches nearer and nearer to the truth as the total concentration of electrolytes in the solution decreases. For electrolytes like silver chloride, which give only ions having a valence of one, it is a fairly good approximation when the concentration is not more than 0.01 or 0.02 *M*. For electrolytes giving ions with valences of two or more, it is a rough approximation down to still smaller concentrations. However, the law is of most use in dealing with very slightly soluble substances and is usually applied to very dilute solutions. When other electrolytes are present, making the law only approximate, it still serves as a valuable guide even if it is not mathematically exact.

The solubility product law can be stated in a more exact form so that it can be used for solutions up to about 1 *M* concentration, and in some cases higher, but this is beyond the scope of the present discussion.

81. Determination of the Solubility Product. Since the solubility product is the product of the concentrations of the ions in a saturated solution, it can be calculated if these concentrations are known. The concentrations of the ions can in some cases be determined by finding the solubility of the substance in pure water. Then if the substance in question is an electrolyte giving only two ions and is assumed to be completely ionized, the molar concentrations of each kind of ion will be equal to the molar concentration of the original salt. The approximate solubility products of a number of slightly soluble salts of interest in qualitative analysis are given in the following table. Not all the values were obtained by the method just outlined. Many substances are not sufficiently soluble. Other complications also enter, so that indirect methods must often be used. Many of the values are only approximate.

TABLE OF SOLUBILITY PRODUCTS

Salt	Ions		Temp. °C.	Solubility Product
	Pos.	Neg.		
AgCl	Ag^+	Cl^-	25	2×10^{-10}
$BaCO_3$	Ba^{++}	CO_3^{--}	25	8×10^{-9}
$BaCrO_4$	Ba^{++}	CrO_4^{--}	18	2×10^{-10}
$BaSO_4$	Ba^{++}	SO_4^{--}	25	1×10^{-10}
$CaCO_3$	Ca^{++}	CO_3^{--}	25	9×10^{-9}
CdS	Cd^{++}	S^{--}	18	4×10^{-29}
CuS	Cu^{++}	S^{--}	18	9×10^{-44}
FeS	Fe^{++}	S^{--}	18	2×10^{-19}
Hg_2Cl_2	Hg_2^{++}	$2Cl^-$	25	4×10^{-18}
HgS	Hg^{++}	S^{--}	25	3×10^{-54}
$MgCO_3$	Mg^{++}	CO_3^{--}	12	3×10^{-5}
$Mg(OH)_2$	Mg^{++}	$2OH^-$	18	1×10^{-11}
$PbCrO_4$	Pb^{++}	CrO_4^{--}	18	2×10^{-14}
PbS	Pb^{++}	S^{--}	18	4×10^{-29}
$PbSO_4$	Pb^{++}	SO_4^{--}	25	2×10^{-8}
ZnS	Zn^{++}	S^{--}	18	1×10^{-23}

82. Precipitation. The solubility product law states the conditions as to ionic concentrations in a saturated solution. For the formation of a precipitate a solution must be at least slightly supersaturated. Therefore, for the formation of a precipitate it is necessary that the product of the molar concentrations of the ions be larger than the solubility product. This might be called the law of precipitate formation.

In a saturated solution of silver chloride at 25°, which contains about 2 mg. of silver chloride per liter, the molar concentrations of silver ion and chloride are 1.4×10^{-5} M. The solubility product therefore is

$$C_{Ag+} \times C_{Cl-} = (1.4 \times 10^{-5}) \times (1.4 \times 10^{-5}) = 2 \times 10^{-10}.$$

If a solution containing chloride ion is added to a solution containing silver ion, and if the product of the concentrations of the ions in the resulting solution is greater than 2×10^{-10}, conditions are right for precipitation. For example, suppose that equal volumes of 0.01 M silver nitrate solution and 0.001 M hydrochloric acid solution are mixed. On mixing, each solution is diluted to twice its former volume, so if no chemical action takes place, the concentrations are decreased to half their former values. The silver nitrate concentration in the resulting solution would be 0.005 M or 5×10^{-3} M and the hydrochloric acid concentration would be 0.0005 M or 5×10^{-4} M. The silver ion concentration would be the same as the silver nitrate concen-

tration, and the chloride ion concentration would be the same as the hydrochloric acid concentration. Multiplying 5×10^{-3} by 5×10^{-4} it is found that the product of the concentrations of the silver and chloride ions would be 2.5×10^{-6}. This is much larger than 2×10^{-10}, so a precipitate would be expected.

Precipitation usually takes place when the law of precipitation would predict it. It does not always do so however, on account of supersaturation. Under some conditions solvents can hold more solute than they could directly dissolve. When this is the case the solution is said to be supersaturated. Precipitation may take place from a supersaturated solution on standing, or may be induced by special means. When precipitation once starts it continues till the solution is just saturated and the conditions as to ionic concentrations are as stated by the solubility product law. Thus, in the above example silver chloride would be precipitated till the product of the concentrations of the ions left in the solution was equal to 2×10^{-10}.

83. The Common Ion Effect. The solubility product law holds not only for solutions in which slightly soluble electrolytes are present alone, but also for saturated solutions in which other electrolytes are present. Let us consider the case in which there is present another electrolyte giving an ion of the same kind as one of those given by the slightly soluble substance. Hydrochloric acid and silver chloride are two such substances, both giving chloride ion in solution.

In a saturated solution containing only silver chloride

$$(C_{Ag^+} \times C_{Cl^-}) = (1.4 \times 10^{-5}) \times (1.4 \times 10^{-5}) = 2 \times 10^{-10}.$$

In such a solution the silver ion concentration is equal to the chloride ion concentration and so is equal to the square root of the solubility product, or 1.4×10^{-5}. Suppose now that hydrochloric acid is added till the chloride ion concentration in the solution is 0.010 M, or 1.0×10^{-2} M. The term C_{Cl^-} in the above equation stands for the *total* chloride ion concentration in the solution. Therefore, the product of the ion concentrations will be, momentarily at least,

$$(C_{Ag^+} \times C_{Cl^-}) = (1.4 \times 10^{-5}) \times (1.0 \times 10^{-2}) = 1.4 \times 10^{-7}.$$

But 1.4×10^{-7} is much larger than 2.0×10^{-10}, the solubility product, and so the solution is supersaturated and precipitation of silver chloride should begin and continue till the ion concen-

tration product no longer exceeds the solubility product. However, it is to be noted that at the moment following the addition of the hydrochloric acid and before the solid precipitate began to form, the solution contained no more silver ion than it did before the hydrochloric acid was added. Therefore, silver chloride must be less soluble in a solution containing chloride ion than it is in pure water. Similarly, silver chloride is less soluble in a solution containing silver ion than it is in pure water. The effect of the presence of an excess of one of the ions of a slightly soluble substance is called the common ion effect.

The common ion effect can be demonstrated conveniently with lead chloride and hydrochloric acid, as in the following experiment. To 10 cc. of lead nitrate solution in a test tube add 5 cc. of 2 *M* hydrochloric acid. Filter, and wash the precipitate twice with distilled water. Disregard any precipitate that forms in the filtrate, which can be thrown away. Next dissolve as much as possible of the precipitate in 5 cc. of distilled water by pouring the water through the filter five times in succession, using two test tubes alternately to catch the solution as it comes through. Finally, add a drop or two of 6 *M* hydrochloric acid to the saturated lead chloride solution thus formed. When chloride ion is added to a saturated solution of lead chloride, a precipitate of the latter is formed. On account of other complications the addition of lead ion (from lead nitrate, for example) will not do the same thing, as would be expected on the basis of the solubility product law alone.

84. The Dissolving of Precipitates. A precipitate placed in a pure solvent or in a solution will continue to dissolve till the solution is saturated with the precipitate. If a solution is not saturated, the product of the concentrations of the ions is smaller than the solubility product. Therefore, if the product of the concentrations of the ions of a slightly soluble substance is less than the solubility product, more of the substance can be dissolved. A substance will continue to dissolve as long as the product of the ion concentrations is less than the solubility product, unless the supply of solid material is exhausted first.

In pure water the product of the concentrations of silver and chloride ions is zero. If solid silver chloride is added, some of it will dissolve. As it dissolves, the product of the ion concentrations will increase till it reaches the value of the solubility

product for silver chloride. After that no more will dissolve. However, if ammonia is present in the solution, it will unite with the silver ion as fast as the latter comes into the solution to form a complex ion.

$$Ag^+ + 2\ NH_3 \rightarrow Ag(NH_3)_2^+ \qquad (92)$$

This will keep the concentration of the silver ion so small that the product of the concentrations of the silver and chloride ions will be less than the solubility product of silver chloride. As long as the ion product is less than the solubility product, silver chloride will dissolve. The result is that a larger amount of silver chloride can be dissolved by an ammonia (ammonium hydroxide) solution than in pure water. This is the basis of the separation of silver and mercury in the silver group. Mercurous chloride will not act this way.

It should be noted that the formation of the silver-ammonia complex ion does not remove *all* the silver ion from the solution. The reaction represented by Equation 92 is reversible. In such solutions the concentration of the chloride ion can be made large enough so that the product of the concentrations of the silver ion and the chloride ion exceeds 2×10^{-10}. Then a precipitate of silver chloride will form.

A simple analogy may help to make clear the dissolving of slightly soluble salts. If a room is full of people, no more can come in. But if a back door is opened and some people go out by it, more can come in by the front door. Any number of people can pass in by the front door if an equal number are at the same time passing out by the back door. Similarly a large amount of silver ion can pass into a solution containing chloride ion, provided that it is taken out again by the formation of a complex ion as fast as it comes in.

Whenever it is possible to remove one of the ions as fast as it comes into a solution, and by so doing keep the ion product less than the solubility product, a slightly soluble substance can be dissolved. An ion can be removed from a solution by adding another ion with which it will unite to form either an undissociated molecule or a precipitate or an insoluble gas. An ion can also be removed by the addition of a substance which will convert it into a complex ion.

Let us consider the case of ferrous sulfide precipitate being dissolved by hydrochloric acid. Ferrous sulfide, like all so-called

insoluble substances, has a small but definite solubility. The dissolved ferrous sulfide gives a small but definite sulfide ion concentration to the solution in which it is dissolved. When acid is added, the sulfide ion unites with hydrogen ion of the acid to form undissociated hydrogen sulfide. This makes the ion product of the ferrous sulfide in the solution less than the solubility product, and more of the solid ferrous sulfide dissolves. But the sulfide ion unites with the hydrogen ion of the acid practically as fast as it comes into the solution, forming undissociated hydrogen sulfide, and most of the hydrogen sulfide formed escapes from the solution as a gas. This keeps the sulfide ion concentration in the solution very small, and the ion product of the ferrous sulfide never becomes as large as the solubility product unless the supply of hydrogen ion is exhausted. In the end either the ferrous sulfide is all dissolved or the acid is all used up.

Most slightly soluble salts of weak acids, that is, acids which are ionized to only a small degree, can be dissolved by strong acids. Examples of such salts are carbonates, sulfides, phosphates and others. When a strong acid is added to such a salt, the concentration of the negative ion of the salt is decreased by its union with the hydrogen ion of the acid to form the undissociated weak acid. This results in the salt being dissolved, as in the case of the ferrous sulfide discussed in the preceding paragraph. Hydroxides can generally be dissolved by acids also, because of the formation of undissociated water, which keeps the hydroxide ion concentration in the solution very small.

A slightly soluble salt of a strong acid, such as silver chloride or barium sulfate, usually cannot be dissolved by another acid. In this case neither of the ions of the slightly soluble substance is removed from the solution when the acid is added. Slightly soluble chlorides and sulfates are not in general dissolved by acids.

QUESTIONS

1. Are most precipitates met in qualitative analysis acids, bases or salts? Name one that is an acid, one that is a base and one that is a salt.

2. Does precipitation and filtration completely remove from the solution the substance precipitated? How might all of a solute be removed from a solution?

3. In a saturated solution of lead sulfate containing no other dissolved substance is there more lead ion or more sulfate ion?

4. If a liter of saturated solution of lead sulfate (Mol. Wt. 303) contains

45 mg. of dissolved solute, compute (*a*) the molar solubility of lead sulfate, (*b*) the molar concentration of the sulfate ion in this solution, (*c*) the molar concentration of the lead ion in this solution, (*d*) the solubility product of lead sulfate.

5. How could it be arranged so that the number of lead and sulfate ions would be unequal in a saturated solution of lead sulfate?

6. Compute the sulfate ion concentration necessary in a 0.02 *M* lead nitrate solution to make the concentration of the lead ions multiplied by the concentration of the sulfate ions equal to the solubility product of lead sulfate. Name some substances that might be used to supply the sulfate ion.

7. What substances when added to solutions of the following would give a pair of substances having a common ion: lead chloride, hydrogen sulfide, calcium sulfate?

8. In which would you expect chloride salts to be more soluble, pure water or 0.01 *M* hydrochloric acid? Why?

9. Why is the precipitate of the hydrochloric acid group washed with hydrochloric acid solution rather than water?

10. Answer the following questions in terms of the solubility product law: (Complete explanations are not required.)

(*a*) Why is zinc ion not in the hydrogen sulfide group?

(*b*) Why is magnesium hydroxide not precipitated in the ammonium sulfide group?

(*c*) Why is copper hydroxide not precipitated along with bismuth hydroxide in the analysis of the copper group?

(*d*) Why is mercuric sulfide not dissolved by dilute nitric acid as the other copper group sulfides are?

(*e*) Why can mercuric sulfide be dissolved by an acid solution containing chlorine?

11. In the separation of barium and calcium ions, why is calcium oxalate dissolved by the acid solution while barium sulfate is not?

12. Why can fairly large amounts of calcium ion and oxalic acid remain in an acid solution together without forming a precipitate, while making the solution basic gives a precipitate of calcium oxalate?

13. Which of the following substances could be expected to be dissolved by a hydrochloric acid solution and which could not; give reasons in each case: AgCl, $CaCO_3$, $Al(OH)_3$, ZnS, $BaSO_4$, CaC_2O_4?

14. Would zinc sulfide be precipitated if a solution 0.01 *M* with respect to zinc ion were saturated with hydrogen sulfide under such conditions that the sulfide ion concentration was 1×10^{-18} *M*?

15. If 1 cc. of 1 *M* potassium chromate were added to 9 cc. of a lead chloride solution to test for lead, what fraction of a gram of lead ion could be present without the formation of a precipitate?

16. The solubility of silver chloride is 2.0×10^{-3} g. per liter at 25° C. Calculate its solubility product?

17. From data given in the table of solubility products calculate the solubility of magnesium carbonate in pure water in grams per liter.

18. State the conditions for precipitation and the dissolving of precipitates in the form that will apply to slightly soluble electrolytes like lead chloride and bismuth sulfide.

CHAPTER XIII

CHEMICAL EQUILIBRIUM

The solubility product law only partially explains many precipitation phenomena. It states that whenever the product of the concentrations of the ions of a slightly soluble substance is greater than the solubility product, the solution is supersaturated, and precipitation is to be expected. However, to apply the law to a particular case, it is necessary to know the values of the ion concentrations in the solution, so that their product can be compared with the solubility product. The concentration of an ion in solution depends upon the concentration of electrolytes which furnish that particular ion, and also upon the extent to which those electrolytes are ionized. The extent of the ionization of many electrolytes is governed by the laws of chemical equilibrium. To understand the theory of qualitative analysis, therefore, it is necessary to understand the laws of chemical equilibrium.

85. Simple Examples of Equilibrium. A simple case of equilibrium is that between water and ice in a mixture containing both. If the mixture is heated, ice will melt. If heat is withdrawn by cooling, water will freeze, forming more ice. These changes can be represented by the equation

$$H_2O \text{ (liquid)} \rightleftarrows H_2O \text{ (solid)} \qquad (93)$$

in which the double arrow indicates that the reaction can go in either direction. When no heat is being added or subtracted, no change takes place in the relative amounts of water and ice. This condition is said to be a condition of equilibrium.

The change represented by Equation 93 does not stop when equilibrium is reached. Water is still changing into ice, and ice is still changing into water, but the two opposite changes go on at equal rates and so counteract each other. Water molecules in the liquid water are continually being deposited on the ice and becoming part of the solid, and water molecules at the surface of the ice are continually leaving to become liquid water molecules.

A condition of equilibrium exists when the number of molecules which go from liquid to solid in a given length of time is exactly equal to the number which go from solid to liquid in the same length of time.

The equilibrium of a solid salt with its saturated solution is similar. A crystal of a salt consists of the ions of the salt arranged in a definite pattern, which can actually be determined with the help of X-rays. When the crystal is placed in water, ions leave the crystal and go into the water forming a solution. Some of the ions return to the crystal from the solution. The more ions there are in the solution, the larger is the number of those returning to the crystal in a given length of time. When the solution is saturated, the rate at which ions return to the crystal is exactly equal to the rate at which ions leave. There is no change in the concentration of ions in the saturated solution as time goes on and the solution is said to be in equilibrium with the crystals. The solubility product law applies to such a solution.

86. Equilibrium in Chemical Reactions. Chemical reactions usually come to equilibrium in a similar manner. If hydrogen and iodine gases are mixed at a temperature in the vicinity of 400° C., they react to form hydrogen iodide. Not all the hydrogen and iodine are converted into hydrogen iodide, however. All three substances, hydrogen, iodine and hydrogen iodide are present when the reaction stops, or rather, appears to stop. For example, if 14.4 cc. each of hydrogen and iodine gases are mixed and heated at 357° C. till equilibrium is attained, there will be in the equilibrium mixture 23.1 cc. of hydrogen iodide and 2.8 cc. each of hydrogen and iodine. If 28.7 cc. of hydrogen iodide is heated to the same temperature, it partially decomposes into hydrogen and iodine, and the resulting mixture is just the same as that resulting from mixing hydrogen and iodine, 23.1 cc. of hydrogen iodide and 2.8 cc. each of hydrogen and iodine. The reaction is reversible, and the equation can be written

$$H_2 + I_2 \rightleftharpoons 2\,HI \qquad (94)$$

Here again the state of equilibrium is thought of, not as a state of rest, but as that state in which the rates of the reactions in the two opposite directions are the same. At the start, when only hydrogen and iodine are present, the reaction toward the

right is fast and there is no reaction toward the left at all. The rate of a chemical reaction increases as the concentrations of the reacting substances increase, or decreases as they decrease. Therefore, as soon as some hydrogen and iodine are used up, their concentrations decrease and the rate of the reaction toward the right becomes slower. Also, as soon as some hydrogen iodide is formed, the reaction toward the left starts, and its rate becomes larger and larger as more and more hydrogen iodide accumulates. It can be seen that finally a point will be reached at which the two rates will be equal. After this there will be no further change in concentrations. When there is no further change in the concentrations as time goes on, equilibrium is said to have been reached.

87. Effect of Pressure, Temperature and Concentration on Equilibrium. When equilibrium is once attained it is permanent as long as there is no change in temperature, pressure, or concentration. If one of these conditions is changed, one of the opposing reactions is usually affected more than the other, so that the system is no longer at equilibrium. However, the reaction immediately proceeds toward a new equilibrium and eventually attains it. When such a change takes place, the equilibrium is said to be altered or shifted. For example, in the case of the equilibrium between hydrogen, iodine and hydrogen iodide as shown in Equation 94 if the temperature is increased, the equilibrium is shifted in such a way as to cause the decomposition of some of the hydrogen iodide and result in a larger proportion of hydrogen and iodine.

A change in temperature nearly always causes a shift in the equilibrium in one direction or the other. A change in pressure sometimes causes a shift in equilibrium and sometimes does not. In qualitative analysis the effects of temperature and pressure on equilibrium are of little importance.

The most important factor from the point of view of qualitative analysis is the concentration. In the case of the reaction of hydrogen and iodine, for example, an increase in the concentration of either hydrogen or iodine temporarily increases the rate of the reaction toward the right. This results in a shift in the equilibrium, because the rate of the reverse reaction is not correspondingly increased till the concentration of hydrogen iodide increases.

The equilibrium of any reversible reaction can be shifted in this way. Assume that equilibrium has been attained in a reaction in which the substances A and B react to form C and D.

$$A + B \rightleftarrows C + D \qquad (95)$$

An increase in the concentration of either A or B will shift the equilibrium in such a way as to give a larger concentration of both C and D. An increase in the concentration of either C or D will shift it in the opposite way. A decrease in one or more of the concentrations will shift the equilibrium also. If some of the substance A in Equation 95 is removed, the rate of the reaction toward the right will be temporarily decreased, and the equilibrium will be shifted to give a greater concentration of B. If the substance D is completely removed as fast as it is formed, the reaction will be unable to come to equilibrium till substances A and B are completely used up. Thus, removing a product makes a reaction go to completion. For example, carbonic acid, H_2CO_3, dissociates into water and carbon dioxide.

$$H_2CO_3 \rightleftarrows H_2O + CO_2 \qquad (96)$$

In this case there is no substance corresponding to B of Equation 95. Carbon dioxide is not very soluble in water and can be completely expelled from a solution by boiling. If a solution of carbonic acid is boiled, carbon dioxide, a product of the dissociation of carbonic acid, is removed from the solution. So the dissociation goes on practically to completion and all the carbonic acid disappears.

88. Mathematical Statement of the Law of Equilibrium. The relation of the state of equilibrium to the concentrations of the reacting substances can be expressed mathematically. Let C_A, C_B, C_C and C_D represent the concentrations of the substances A, B, C and D respectively, in Equation 95. Repeating in mathematical language what has already been said concerning the velocity of a reaction, the velocity of the reaction toward the right, v_1, is proportional to C_A and C_B and so is equal to some number, k_1, times the product of C_A and C_B,

$$v_1 = k_1 \times C_A \times C_B$$

Similarly in the case of the velocity of the reaction in the opposite direction, v_2,

$$v_2 = k_2 \times C_C \times C_D$$

At equilibrium v_2 and v_1 are equal, and so

$$k_2 \times C_C \times C_D = k_1 \times C_A \times C_B$$

Rearranging

$$\frac{C_C \times C_D}{C_A \times C_B} = \frac{k_1}{k_2} = K$$

where K is a number, equal to k_1 divided by k_2, which is called the equilibrium constant. The constant, K, may vary with the temperature and pressure, but should not vary when the concentrations vary.

If the value of C_C is increased, the left hand term of the above mathematical equation is temporarily increased in value. The left hand term will consequently exceed the constant, and a reaction must take place; the substances C and D must react to form A and B. This decreases the numerator and increases the denominator of the left hand term of the equation so that the left hand term becomes equal to the constant again. After this, the concentrations of the reacting substances undergo no further change unless another concentration is altered by an outside agency. A decrease in the concentration of either C or D would favor the opposite reaction; more of C and D would be formed. Likewise alteration of the concentration of either A or B would cause a shift in the equilibrium.

The above is a rather simple case in that a number of molecules of A react with an equal number of molecules of B to produce the same number of molecules of both C and D. Or, in other words, for every gram molecular weight, or mole, of A which reacts, one of B reacts and one each of C and D are formed. In the case of a reaction which may be designated by the equation

$$mA + nB \rightleftarrows pC + qD \qquad (97)$$

in which m, n, p, and q stand for simple whole numbers representing the relative numbers of molecules reacting, the equilibrium expression is

$$\frac{(C_C)^p \times (C_D)^q}{(C_A)^m \times (C_B)^n} = K$$

An examination of this equation will show that the effects of changes in concentration in the case of a reaction such as this

will be qualitatively the same as in the case of the simpler reactions. The above mathematical expressions are more or less approximately true but are not exact. The law of equilibrium can be stated in an exact form, but this cannot be taken up here.

89. Precipitation by Hydrogen Sulfide. Many illustrations of the effects of concentration changes can be found in qualitative analysis. The ionization of the weak electrolyte hydrogen sulfide is a reversible chemical reaction.

$$H_2S \rightleftarrows 2\ H^+ + S^{--} \qquad (98)$$

The reaction is such that at equilibrium only very small concentrations of hydrogen and sulfide ions are present. When hydrochloric acid is added to a solution of hydrogen sulfide, the hydrogen ion concentration in the solution is greatly increased. This is because the total amount of hydrogen ion in the solution is equal to the sum of the hydrogen ion from the largely ionized hydrochloric acid and that from the hydrogen sulfide. Since Reaction 98 is a reversible reaction, an increase in the hydrogen ion concentration shifts the equilibrium in such a way as to use up hydrogen ion and with it sulfide ion also. The result is a decrease in the sulfide ion concentration. That is, in a hydrogen sulfide solution the more hydrochloric acid added, the smaller the sulfide ion concentration will be. This is the reason why hydrochloric acid is added before the precipitation of the hydrogen sulfide group, and why care must be taken that a definite concentration of acid, 0.25 *M* to 0.3 *M*, is present. The sulfide ion concentration must be reduced so low that even if fairly large concentrations of the ammonium sulfide group ions are present the solubility products of their sulfides are not exceeded. The sulfide ion concentration must not be decreased too much, however, because it is necessary that all the solubility products of the hydrogen sulfide group sulfides be exceeded, even when only small amounts of those ions are present in the solution. Thus, in the precipitation of the hydrogen sulfide group it is desired that cadmium sulfide with a solubility product of 3.6×10^{-29} be completely precipitated, while at the same time the sulfide ion concentration is kept too low to precipitate zinc sulfide, which has a solubility product of 1.2×10^{-23}.

Reaction 98 really is the resultant of two reactions.

$$H_2S \rightleftharpoons H^+ + HS^- \quad (99)$$

$$HS^- \rightleftharpoons H^+ + S^{--} \quad (100)$$

Hydrogen sulfide ionizes to give hydrogen ion and hydrosulfide ion, HS^-, and the latter ionizes further to give another hydrogen ion and sulfide ion. The total change might be written

$$H_2S \rightleftharpoons H^+ + HS^- \rightleftharpoons 2\,H^+ + S^{--} \quad (101)$$

In the case of precipitation by hydrogen sulfide it is only the sulfide ion concentration which is of significance, and it makes little difference whether or not the intermediate step in the ionization is considered. In some cases the intermediate step needs to be taken into account. More of the total hydrogen sulfide exists in the form of hydrogen and hydrosulfide ions than in the form of hydrogen and sulfide ions.

90. Sodium and Ammonium Sulfides. When sodium hydroxide is added to a solution of hydrogen sulfide, or vice versa, hydrogen ion and hydroxide ion tend to unite to form water. Examination of Equation 101 will show that removal of hydrogen ion will tend to make the reaction go to the right, using up molecular hydrogen sulfide and forming more hydrosulfide and sulfide ions. If only a limited amount of sodium hydroxide is added, Equation 100 is relatively little affected and only a small amount of sulfide ion is present. The reaction represented by Equation 99 is the one most affected. As more sodium hydroxide is added, the further ionization of the hydrosulfide ion is favored by the removal of the hydrogen ion of Equation 100. However, the hydrosulfide ion has such a small tendency to ionize further that only a relatively small part of it ionizes, even under the influence of an excess of sodium hydroxide. Such a solution would be a mixture of sodium hydrosulfide and sodium hydroxide, with some sodium sulfide. Nevertheless, such a solution is usually called a sodium sulfide solution.

Ammonium hydroxide is a weaker base than sodium hydroxide. When it is added to a hydrogen sulfide solution it does not remove the hydrogen ion to even as great an extent as sodium hydroxide does. Therefore, the sulfide ion concentration in an ammonium sulfide solution is much smaller than that in a sodium sulfide solution. It is of course much larger than that in a hydrogen sulfide solution containing hydrochloric acid. The following

table shows the approximate sulfide, hydrosulfide and hydrogen ion concentrations in various solutions. It is to be noted that all three of these ions are present in each of the solutions. That is because of the reversible reactions expressed by Equations 99 and 100.

SULFIDE, HYDROSULFIDE, AND HYDROGEN ION CONCENTRATIONS IN SULFIDE SOLUTIONS

Solution	Molar Concentration at 25° C.		
	H^+	HS^-	S^{--}
Na_2S, 1 M	1×10^{-14}	0.91	0.09
$(NH_4)_2S$, 1 M	5×10^{-10}	1	2×10^{-6}
H_2S, saturated	1×10^{-4}	1×10^{-4}	1×10^{-15}
H_2S, saturated + 2 M acetic acid	6×10^{-3}	2×10^{-6}	3×10^{-19}
H_2S, saturated + 0.3 M HCl	0.3[a]	4×10^{-8}	2×10^{-22}

[a] The hydrogen ion in a solution of this concentration acts as if its concentration were 0.23 M.

The figures in the table can be used to show why the sulfides of the hydrogen sulfide group can be precipitated in an acid solution while those of the ammonium sulfide group cannot. Consider copper ion as a typical member of the hydrogen sulfide group and ferrous ion as a typical member of the ammonium sulfide group. Assume that both ions are present in a solution and that each has a concentration of 0.01 M. Assume also that hydrochloric acid equivalent to 5 cc. of 6 M acid is present per 100 cc., as in a solution ready for the precipitation of the hydrogen sulfide group. The hydrogen ion concentration of the solution is 0.3 M, and if the solution is saturated with hydrogen sulfide, the sulfide ion concentration is 2×10^{-22} according to the table. If the product of the concentrations of the copper and sulfide ions is greater than the solubility product of copper sulfide, a precipitate is to be expected. The product of 0.01 and 2×10^{-22} is 2×10^{-24} which is much larger than the solubility product of copper sulfide, which is 9×10^{-44}. However, the product of 0.01 and 2×10^{-22} is less than the solubility product of ferrous sulfide, which is 2×10^{-19}, so ferrous sulfide cannot be formed. On the other hand if a solution containing ferrous ion at a concentration of 0.01 M is made 1 M with respect to ammonium sulfide, the ion product for ferrous sulfide will be $0.01 \times 2 \times 10^{-6} = 2 \times 10^{-8}$, which greatly exceeds the solubility product. Therefore, ferrous sulfide should be precipitated by ammonium sulfide, but not by hydrogen sulfide in a solution in which the hydrogen ion concentration is 0.3 M.

91. Equilibrium Between Water and Its Ions. Another equilibrium of importance is that between water and its ions.

$$H_2O \rightleftharpoons H^+ + OH^- \qquad (102)$$

The amount of water ionized is very small. The concentrations of hydrogen and hydroxide ions in pure water are only 1.0×10^{-7} mole per liter at 25°. This concentration is equivalent to 1 g. of hydrogen ion in 10,000 tons of pure water. If a base is added to water, the hydroxide ion concentration is increased, and so the hydrogen ion concentration must decrease by union with hydroxide ion. When the new equilibrium is established, the hydrogen ion concentration is less than before, but it is not zero. Hence, a basic solution is not one which contains hydroxide ions and no hydrogen ions, but one in which the hydroxide ion concentration is larger than the hydrogen ion concentration. Likewise an acid solution is a solution in which the hydrogen ion concentration is the larger.

When ammonia (NH_3) is added to water, it dissolves, and part of it unites with the hydrogen ion of the water to form ammonium ion.

$$NH_3 + H^+ \rightleftharpoons NH_4^+ \qquad (103)$$

This removal of hydrogen ion to form ammonium ion causes water molecules to dissociate to form more hydrogen and hydroxide ions; the reaction represented by Equation 102 goes from left to right. Consequently the hydroxide ion concentration of the solution increases, and the resulting ammonium hydroxide solution is basic.

It is to be noted that not all of the ammonia combines with hydrogen ion. Ammonium hydroxide solutions always contain free ammonia as well as ammonium ion, hydroxide ion and hydrogen ion. It is the free ammonia, NH_3, escaping from the solution which gives an ammonium hydroxide solution its characteristic odor. When the hydrogen ion concentration is greatly increased by the addition of an acid, Reaction 103 goes from left to right almost completely, giving an ammonium salt. Solutions of ammonium salts of strong acids do not contain much free ammonia, and they have no odor of ammonia. This is not true of ammonium salts of weak acids on account of what is known as hydrolysis.

92. Hydrolysis. In dissolving sodium carbonate in water, sodium and carbonate ions are added to a solution already containing very small concentrations of hydrogen and hydroxide ions. A reaction then takes place between hydrogen ion and carbonate ion to form bicarbonate ion, HCO_3^-, and carbonic acid, H_2CO_3.

$$H^+ + CO_3^{--} \rightleftarrows HCO_3^- \qquad (104)$$

$$2\,H^+ + CO_3^{--} \rightleftarrows H_2CO_3 \qquad (105)$$

This removal of hydrogen ion allows further ionization of water, furnishing more hydrogen ion for Reactions 104 and 105 and causing the accumulation of more hydroxide ion in the solution than there is hydrogen ion, because the hydroxide ion of the water is not removed. Consequently the solution is basic. That this is actually the case can be seen by testing a sodium carbonate solution with litmus. This behavior is characteristic of salts formed from weak acids and strong bases. Hydrolysis in such cases usually does not go very far because the accumulation of the hydroxide ion soon makes the hydrogen ion concentration too small for further reaction. In the case of sodium sulfide, however, it takes place to a large extent, as the above table of sulfide ion concentrations shows.

Salts formed from strong acids and weak bases act in the opposite manner. Aluminum nitrate can be taken as an example of this class of salts. Aluminum nitrate can be considered as formed by the reaction of nitric acid and aluminum hydroxide. The latter is a weak base, that is, it exists partly in the form of hydrogen and aluminate ions (see Equation 64, page 64) and perhaps partly in the entirely non-ionized form. So in an aluminum nitrate solution the aluminum ion reacts with some of the hydroxide ion (from the water) and removes it from the solution, leaving the solution acid. In this case also, hydrolysis does not usually go very far because the accumulation of hydrogen ion makes the hydroxide ion concentration too low for further reaction with the aluminum ion.

When both the acid and the base from which a salt can be considered to have been formed are weak, hydrolysis is much more pronounced. In such a case both of the ions of water are removed from the solution at the same time, and neither is made small by the accumulation of the other. Of course the ions

removed are replaced by the dissociation of more water. Ammonium sulfide is a salt of a weak base and a strong acid, and the above table shows that it contains much less sulfide ion than does sodium sulfide.

Hydrolysis can become practically complete in some cases. This sometimes happens when a precipitate is formed. For example, when aluminum sulfide is brought into water it dissolves to a certain extent. Part of the sulfide ion unites with hydrogen ion of the water, and the hydroxide ion concentration of the water is made large enough so that the solubility product of aluminum hydroxide is exceeded. Consequently aluminum hydroxide is precipitated. Hydrolysis in this case is practically complete. Chromium sulfide would behave in the same way. It can now be understood why aluminum and chromium ions do not form sulfides, but precipitate as hydroxides, in the precipitation of the ammonium sulfide group.

An example of hydrolysis is sometimes seen in qualitative analysis when the filtrate from the chloride group is diluted with water previous to precipitation with hydrogen sulfide. If antimony ion, Sb^{+++}, is present, for example, it can form a precipitate of antimony oxychloride, SbOCl.

$$Sb^{+++} + 2\ OH^- + Cl^- \rightleftarrows SbOCl + H_2O \qquad (106)$$

If antimony trichloride is brought into water, there is enough hydroxide ion present so that the solubility product of antimony oxychloride is exceeded and the precipitate results. To prevent the precipitation of antimony oxychloride it is only necessary to add hydrochloric acid to reduce the hydroxide ion concentration so that the solubility product is not exceeded. To prepare a clear solution of antimony trichloride from the solid salt it is necessary to add some hydrochloric acid to prevent hydrolysis. Arsenic, bismuth, tin, mercurous and other salts behave similarly.

93. Complex Ions. Sometimes ions of two different kinds, or an ion and an undissociated molecule can unite to form what is called a complex ion. Several examples of complex ions are met in qualitative analysis. The formation of some of these is represented by the following equations.

$$Ag^+ + 2\ NH_3 \rightleftarrows Ag(NH_3)_2^+ \qquad (107)$$

$$Cu^{++} + 4\ NH_3 \rightleftarrows Cu(NH_3)_4^{++} \qquad (108)$$

$$Zn^{++} + 4\ NH_3 \rightleftarrows Zn(NH_3)_4^{++} \quad (109)$$

$$As_2S_5 + 3\ S^{--} \rightleftarrows 2\ AsS_4^{---} \quad (110)$$

Complex ions are usually in equilibrium with the ions, or ions and molecular species, from which they are formed, although in some cases the amounts of the constituents at equilibrium are extremely small. In the cases given above, appreciable amounts of the constituent ions and molecules are present at equilibrium.

Complex ions have properties different from those of the ions and molecules from which they are formed. Thus, the copper-ammonia ion differs in color from copper ion, and does not form a hydroxide precipitate as copper ion does.

A solution containing a complex ion shows the properties of the constituent substances in so far as the small amounts of the constituent substances present allow. In the case of the copper-ammonia complex ion there is so little copper ion present that the product of its concentration and that of the hydroxide ion of an excess of ammonium hydroxide is less than the solubility product. However, the solubility product of copper sulfide is so very small that if ammonium sulfide is added to a solution containing the complex ion, a precipitate of copper sulfide results. The zinc-ammonia complex ion acts similarly. A solution of silver-ammonia complex ion will not give a precipitate of silver chloride unless a large amount of chloride ion is added, but it will easily give a precipitate of silver sulfide.

When a precipitate is formed involving an ion which is in equilibrium with a complex ion, that particular ion is partially removed from the solution. This favors the dissociation of the complex ion, and the dissociation will continue as long as the precipitation continues. Thus if a zinc-ammonia complex ion is in equilibrium with zinc ion and ammonia, as shown in Equation 109, and some ammonium sulfide is added, the zinc ion unites with sulfide ion to give a precipitate of zinc sulfide. This necessitates dissociation of the complex ion, and the final result is that all the zinc in the complex ion is converted into zinc sulfide. It all must pass through the intermediate step of existing momentarily at least as zinc ion, but as long as sulfide ion is present in sufficient quantity the zinc ion is removed as fast as it is formed.

Any complex ion can be decomposed if the concentration of one

of the simpler substances into which it dissociates can be reduced sufficiently. In the case of the ammonia complexes this can be done either by precipitating out the metallic ion or by adding an acid, the hydrogen ion of which converts the ammonia into ammonium ion. The thioarsenate ion of Equation 110 can be decomposed by the addition of hydrogen ion, the sulfide ion being converted into hydrosulfide ion and hydrogen sulfide, and so removed from the field of action.

Some complex ions have in equilibrium with them such very small concentrations of their constituents that the presence of the latter cannot be detected. A solution containing ferrocyanide ion, $Fe(CN)_6^{----}$, does not give any test for ferrous ion, although it can be formed from ferrous ion and cyanide ion, CN^-. Likewise ferricyanide ion, $Fe(CN)_6^{---}$, does not give enough ferric ion to give a test. Such complex ions as these are very stable as compared with those considered above.

94. Equilibrium in Double Decompositions. When two substances such as sodium chloride and sulfuric acid are mixed in dilute solution no evidence of a reaction, such as precipitation or a temperature change, is apparent.

$$NaCl + H_2SO_4 \leftrightharpoons NaHSO_4 + HCl \qquad (111)$$

From Equation 111 it might be inferred that equilibrium had set in. The application of the theory of ionization gives a different view, however. All four substances are strong electrolytes and therefore are ionized in solution.

$$Na^+ + Cl^- + H^+ + HSO_4^- \leftrightharpoons Na^+ + HSO_4^- + H^+ + Cl^- \qquad (112)$$

The ionic equation indicates that no reaction has taken place; the products are no different from the reacting substances.

Under certain conditions, however, there is a tendency for a reaction to take place when the ions shown in Equation 112 are mixed. If concentrated sulfuric acid is added to a concentrated solution of sodium chloride, gaseous hydrogen chloride is formed, especially if the mixture is boiled.

$$Na^+ + Cl^- + H^+ + HSO_4^- \rightarrow HCl\uparrow + Na^+ + HSO_4^- \qquad (113)$$

The ions which appear on both sides of the equation can be omitted giving the simpler Equation 114.

$$H^+ + Cl^- \rightarrow HCl\uparrow \qquad (114)$$

Removal of gaseous hydrogen chloride, by boiling for example, allows the reaction to proceed practically to completion. Similar reactions have been met before in the "fuming off" process, for example in the analysis of the alkali group, page 80.

If concentrated solutions of hydrochloric acid and sodium acid sulfate are mixed, sodium chloride is precipitated and sulfuric acid remains in solution.

$$Na^+ + Cl^- \rightarrow NaCl\downarrow \qquad (115)$$

Whenever as the result of mixing two ionized substances a gas can form and escape, or a precipitate can form, a double decomposition takes place. Most of the precipitation reactions of qualitative analysis are reactions of the latter type. The solubility product law, rather than the law of chemical equilibrium applies to precipitation reactions.

Neutralization reactions form another class of double decompositions. When sodium hydroxide and hydrochloric acid are mixed, a reaction between hydrogen and hydroxide ions to form water takes place.

$$Na^+ + OH^- + H^+ + Cl^- \rightarrow Na^+ + Cl^- + H_2O \qquad (116)$$

$$H^+ + OH^- \rightleftarrows H_2O \qquad (117)$$

The reaction is reversible in so far as water is ionized. The reaction consists of the formation of water from its ions, and the law of chemical equilibrium applies to this.

The reaction between a strong acid and the salt of a weak acid is quite similar. For example, sodium acetate is a salt of the weak acetic acid and it reacts with hydrochloric acid to form non-ionized acetic acid.

$$Na^+ + C_2H_3O_2^- + H^+ + Cl^- \rightarrow HC_2H_3O_2 + Na^+ + Cl^- \qquad (118)$$

$$C_2H_3O_2^- + H^+ \rightleftarrows HC_2H_3O_2 \qquad (119)$$

In this case the little ionized acetic acid is formed from its ions. The reaction is less nearly complete than in the case of the formation of water, because acetic acid is appreciably ionized and the ions will come to equilibrium with the non-ionized acetic acid. Whenever a slightly ionized substance can be formed as the result of mixing two ionized substances, a reaction will take place.

QUESTIONS

1. Describe the effect of adding hydrogen gas to a mixture of hydrogen, iodine and hydrogen iodide at equilibrium.

2. Describe the effect of adding hydrochloric acid solution to a hydrogen sulfide solution.

3. Why is it undesirable to have the hydrogen ion concentration too large in the precipitation of the hydrogen sulfide group.

4. Would cadmium ion be precipitated as the sulfide more completely from a solution 1 *M* with respect to ammonium sulfide than from a solution which was 0.3 *M* with respect to hydrochloric acid and saturated with hydrogen sulfide?

5. Explain why nickel ion belongs to the ammonium sulfide group rather than to the hydrogen sulfide group.

6. Would the addition of sulfuric acid to a hydrogen sulfide solution lower the sulfide ion concentration? Give reason.

7. How could you obtain a solution
   (*a*) having a large hydrogen ion concentration,
   (*b*) having an extremely small hydrogen ion concentration,
   (*c*) in which the hydrogen and hydroxide ion concentrations were equal,
   (*d*) having as large a sulfide ion concentration as possible,
   (*e*) having an extremely small sulfide ion concentration,
   (*f*) with a hydroxide ion concentration only slightly larger than the hydrogen ion concentration?

8. Why does an ammonium hydroxide solution smell of ammonia while an ammonium chloride solution does not?

9. If a solution containing zinc-ammonia complex ion and chloride ion were boiled, would the zinc ion concentration be increased?

10. Carbonic acid in solution is in equilibrium with carbon dioxide and water. Carbon dioxide is not very soluble in water. Show what would happen on the addition of hydrochloric acid to sodium carbonate.

11. Give two reasons why most carbonates are dissolved easily by strong acids such as nitric, hydrochloric or sulfuric acid.

12. Explain why a slightly soluble salt of a weak acid can be dissolved by a strong acid.

13. Explain why a slightly soluble salt of a strong acid cannot in general be dissolved by a strong acid.

14. Express the equilibrium conditions for the ionization of water. Explain what effect an increase in hydrogen ion concentration would have on the hydroxide ion concentration. An increase in hydrogen ion concentration in water could be caused by the addition of an acid.

CHAPTER XIV

OXIDATION–REDUCTION REACTIONS

Many oxidation-reduction reactions are met in qualitative analysis. For example, when hydrogen sulfide is added to a solution containing ferric ion, sulfide ion is oxidized and ferric ion is reduced as indicated by the equation

$$2\ Fe^{+++} + S^{--} \rightarrow 2\ Fe^{++} + S\downarrow \qquad (120)$$

In the separation of copper ion from cadmium ion the former is reduced to metallic copper by metallic iron, which is oxidized to ferrous ion.

$$Cu^{++} + Fe \rightarrow Cu\downarrow + Fe^{++} \qquad (121)$$

It is the purpose of this chapter to show something of the nature of oxidation and reduction and to show how this knowledge can be used in balancing equations for the more complicated oxidation-reduction reactions.

95. The Structure of Atoms. In order to better understand oxidation and reduction in ionic reactions it is desirable to have in mind some of the newer ideas of the structure of atoms and ions. Atoms are believed to be built up of only two different kinds of substances, protons and electrons. A proton is a small body which has a mass approximately equal to that of the hydrogen atom. It is a unit of positive electricity. The number of protons in an atom determine its atomic weight, the more protons the larger the atomic weight. Electrons are units of negative electricity. An electron has much less mass than a proton, only one two thousandth as much. The electrical charge of an electron is equal to the electrical charge of a proton.

Atoms may be said to consist of two parts, the nucleus and the electrons outside the nucleus, which may be called the space electrons. The nucleus is thought of as being at the center of the atom, with the space electrons surrounding it and in motion about it. The nucleus is composed of both protons and electrons, which are probably packed very close together. The number of protons in the nucleus is always greater than the number of

electrons, hence the nucleus is always positively charged. The number by which the protons exceed the electrons in the nucleus of any atom is its *atomic number*. In any neutral atom the number of space electrons is numerically equal to the atomic number. Therefore, in a complete (or neutral) atom the total number of electrons is equal to the total number of protons; the amount of negative electricity is equal to the amount of positive electricity. The relation of the nucleus to the space electrons may be thought of as somewhat similar to the relation of the sun to the earth and other planets revolving around it. The nucleus is analogous to the sun and the space electrons to the planets.

96. Positive Ions. The atoms of many of the elements can part with one or more of their electrons and can get along without them under certain conditions. When this happens, the positive electrical charge of the nucleus will not be balanced by the total negative electrical charge of the electrons around the nucleus. Therefore, the part of the atom remaining will bear a positive charge. This is what we know as a positive ion. Thus, a hydrogen ion is a hydrogen atom which has lost one electron. When gaseous hydrogen chloride, HCl, dissolves in water, the hydrogen atom splits off from the chlorine atom but leaves an electron behind. The solution then contains positive hydrogen ions and negative chloride ions. An atom of zinc can lose two electrons, becoming a zinc ion, Zn^{++}. When metallic zinc, consisting of zinc atoms, is placed in a hydrochloric acid solution, the zinc atoms give electrons to hydrogen ions, and become zinc ions.

$$Zn + 2\ H^+ \rightarrow Zn^{++} + H_2\uparrow \qquad (122)$$

Hydrogen atoms are formed when the hydrogen ions get back their lost electrons. They then combine in pairs and escape as gaseous hydrogen.

97. The Electromotive Series. The elements which can lose electrons and form positive ions are the metals. Most of the common metals can react as zinc does, forming the corresponding metallic ions and liberating hydrogen gas. Some, like the alkali metals, react very vigorously. Others, like tin and lead, react with difficulty, and the reaction proceeds slowly. A few metals, like copper and silver, cannot give up electrons to hydrogen ions at all. However, they will react with other substances, nitric

acid for example, and part with electrons to form positive ions. Thus, metals differ from each other as to the ease with which they can lose electrons, and their chemical behavior is related to this property.

The names of the metals can be arranged in a vertical column or series. At the top of the column are placed the names of those metals which lose their electrons most easily, and consequently are most active chemically. Coming down the column the metals listed decrease in their chemical activity and increase in the firmness with which they retain their electrons. The metals listed at the bottom of the column are the least active chemically. This arrangement is called the electromotive series or displacement series.

ELECTROMOTIVE SERIES

Potassium
Sodium
Barium
Calcium
Magnesium
Zinc
Iron
Cadmium
Nickel
Tin
Lead
Hydrogen
Bismuth
Copper
Antimony
Mercury
Silver
Gold
Platinum

Ions of any of the metals in the series can take electrons from metals higher up in the series, but not from metals below them. Thus antimony ion, Sb^{+++}, can take electrons from metallic iron to give metallic antimony and ferrous ion, but ferrous ion cannot take electrons from metallic antimony.

$$2\ Sb^{+++} + 3\ Fe \rightarrow 3\ Fe^{++} + 2\ Sb\downarrow \qquad (123)$$

Another way of saying the same thing is that metallic iron will displace antimony but antimony metal will not displace iron, hence the name displacement series. The reaction between antimony ion and metallic iron is the one used to precipitate antimony from the solution in the analysis of the tin group.

98. Negative Ions. In general, only the metallic elements form positive ions. The non-metallic elements, of which chlorine can be taken as an example, have the property of taking up extra electrons to form negatively charged atoms or groups of atoms which are called negative ions. Thus, chlorine when passed into a basic solution gives chloride ion and hypochlorite ion.

$$Cl_2 + 2\ OH^- \rightarrow Cl^- + ClO^- + H_2O \qquad (124)$$

Hypochlorite ion is a group of two atoms possessing as a group one more electron than it has protons and so is negatively charged. Other examples of groups bearing negative charges are sulfate ion, SO_4^{--}, nitrate ion, NO_3^-, and phosphate ion, PO_4^{---}.

99. Oxidation-Reduction Reactions. Let us consider ferrous and ferric ions in the light of the above. Ferrous ion, Fe^{++}, is iron which has lost two electrons per atom, and ferric ion, Fe^{+++}, is iron which has lost three electrons per atom. The change of ferric ion to ferrous ion involves merely the addition of one electron. When ferric ion comes in contact with a substance from which it can take electrons it becomes ferrous ion by taking up one electron per ion, or in extreme cases it may become metallic iron by taking up three electrons per ion. As shown in Equation 120, ferric ion can take electrons from sulfide ion. Sulfide ion is negatively charged; that is, each sulfide ion has two extra electrons. The two ferric ions are converted into ferrous ions, and the sulfide ion, losing both its extra electrons, becomes sulfur.

A reaction of this type is called an oxidation-reduction reaction. In the case of reactions between electrolytes in water solution we may define oxidation as the loss of electrons by atoms or ions and reduction as the gain of electrons by atoms or ions. An oxidizing agent is a substance which can cause loss of electrons (oxidation), and a reducing agent is a substance which can cause a gain of electrons (reduction). In Equation 120 sulfide ion is the reducing agent while ferric ion is the substance reduced. Or, we might say that sulfide ion is oxidized and ferric ion is the oxidizing agent. Oxidation and reduction must necessarily occur together, oxidation to supply the electrons which are required for reduction.

The reactions represented by Equations 122 and 123 are oxidation-reduction reactions. Metals are reducing agents, that is, they are easily oxidized. An atom of a metal must give up one

or more electrons in becoming an ion. In the electromotive series the metals are arranged in the order of their strength as reducing agents, the strongest at the top.

100. Equilibrium in Oxidation-Reduction Reactions. Oxidation-reduction reactions always come to an equilibrium, although often the reaction is so nearly complete that it can be considered complete for practical purposes. The reaction between ferrous ion and iodine is reversible and comes to equilibrium.

$$2\ Fe^{++} + I_2 \rightleftarrows 2\ Fe^{+++} + 2\ I^- \qquad (125)$$

The law of chemical equilibrium can be applied to oxidation-reduction reactions. In the case of the above reaction the removal of ferric ion from the system would make the reaction more nearly complete. On the other hand, the removal of iodine would favor the reaction toward the left, making the oxidation of the ferrous ion less complete.

Writing Equations for Oxidation-Reduction Reactions

101. Balancing Equations by Inspection. Equations for the simpler oxidation-reduction reactions can be written by inspection. For example, chlorine, Cl_2, can oxidize ferrous chloride to ferric chloride.

$$2\ FeCl_2 + Cl_2 \rightarrow 2\ FeCl_3 \qquad (126)$$

The ionic form of this equation is also easy to balance.

$$2\ Fe^{++} + Cl_2 \rightarrow 2\ Fe^{+++} + 2\ Cl^- \qquad (127)$$

The ferrous ions give up one electron each to the chlorine atoms. A positive charge results when an atom or ion loses an electron.

Equation 123 above is another example of an equation easily balanced by inspection. If desired, it can be put into the molecular form by merely replacing each positive charge by a chlorine atom, or in other words, by adding six chloride ions to each side of the equation and writing them as if combined with the antimony and ferrous ions, respectively.

$$2\ SbCl_3 + 3\ Fe \rightarrow 3\ FeCl_2 + 2\ Sb\downarrow \qquad (128)$$

This equation could be easily balanced by inspection in this form.

102. Balancing the Less Simple Equations. Other equations are not so easily balanced. An example of such an equation has

been given on page 46, namely Equation 29. It is the purpose of this section to show a method by which the less simple oxidation-reduction equations can be balanced.

It is necessary to know the formulas of all the reacting substances and products of a reaction before the equation can be written. The composition of the products of a particular reaction is to be decided only by experiment. Fortunately a large number of such experiments have been made and the results have been recorded in books. The products of most of the common reactions can be found in books if they are not known from experience. When the formulas of the initial and final products are known, the key to balancing an oxidation-reduction equation lies in knowing how many electrons are given up by the reducing agent and how many are taken by the oxidizing agent. The amounts of the two substances must be so adjusted that the total number of electrons given up in the oxidation of the one substance exactly equals the total number taken by the reduction of the other. Some examples will make this clear.

While actually neither oxidation nor reduction can take place alone, it is sometimes convenient to write equations as if they did. Thus, for the reaction of ferric ion and sulfide ion we can write what might be called partial equations.

$$Fe^{+++} + (-) \rightarrow Fe^{++} \qquad (129)$$

$$S^{--} \rightarrow S\downarrow + 2\,(-) \qquad (130)$$

The symbol $(-)$ is used to indicate an electron. If Equation 129 is multiplied through by 2 and added to Equation 130, the free electrons will cancel, there being equal numbers of electrons on both sides of the equation.

$$2\,Fe^{+++} + 2\,(-) + S^{--} \rightarrow 2\,Fe^{++} + S\downarrow + 2\,(-) \qquad (131)$$

When the electrons are cancelled Equation 120 is obtained. If it is desired to change the equation to the molecular form the ferric ion can be replaced by ferric chloride and the sulfide ion by hydrogen sulfide. The products will be ferrous chloride, hydrochloric acid and sulfur.

$$2\,FeCl_3 + H_2S \rightarrow 2\,FeCl_2 + 2\,HCl + S\downarrow \qquad (132)$$

A somewhat more complicated equation is that for the reduction of dichromate ion, $Cr_2O_7^{--}$, by sulfide ion in an acid solution. If dichromic acid is present in a solution being analyzed, this reaction takes place when the hydrogen sulfide group is being precipitated. Chromic ion, Cr^{+++}, is a product of the reaction, as are also water and sulfur. Partial equations can be written as before, one for the reduction of the dichromate ion, with the help of hydrogen ion, and one for the oxidation of the sulfur.

$$Cr_2O_7^{--} + 14\ H^+ + 6\ (-) \rightarrow 2\ Cr^{+++} + 7\ H_2O \quad (133)$$

$$S^{--} \rightarrow S\downarrow + 2\ (-) \quad (134)$$

In Equation 133 enough hydrogen ions are taken to unite with all the oxygen of the dichromate ion to form water. This is done because the ion resulting, Cr^{+++}, contains no oxygen and no other disposal of the oxygen would be in accord with the facts. When the partial equation is balanced with respect to atoms, it must be balanced with respect to electrical charges. In doing this it can be assumed that a positive charge and a negative charge on the same side of the equation cancel each other. There are 6 positive charges on the right hand side of Equation 133 and $14 - 2 = 12$ positive charges on the left hand side. To make a net total of 6 positive charges on the left hand side, 6 electrons have to be added.

If Equation 134 is now multiplied by 3 in order to give 6 electrons, the two equations can be added and the electrons can be cancelled out.

$$Cr_2O_7^{--} + 14\ H^+ + 3\ S^{--} \rightarrow 2\ Cr^{+++} + 7\ H_2O + 3\ S\downarrow \quad (135)$$

To obtain the molecular equation from this, it is necessary to add certain ions to each side of the equation. Assuming that the original reacting substances were potassium dichromate, hydrochloric acid and hydrogen sulfide, it is apparent that 2 potassium ions are needed for one dichromate ion and that a certain number of chloride ions (or other negative ions) must be added to balance the hydrogen ions. Since 6 of the 14 hydrogen ions can be combined with the 3 sulfide ions, 8 remain unbalanced and so 8 chloride ions are needed. Therefore, adding 2 potassium ions and 8 chloride ions to each side of the equation should allow writing the left side entirely in the molecular form. If Equation

135 is balanced, the above procedure must allow writing the right side in molecular form also.

$$2\ K^+ + Cr_2O_7^{--} + 8\ H^+ + 8\ Cl^- + 3\ H_2S \rightarrow 2\ Cr^{+++} + 8\ Cl^- + 2\ K^+ + 7\ H_2O + 3\ S\downarrow \quad (136)$$

$$K_2Cr_2O_7 + 8\ HCl + 3\ H_2S \rightarrow 2\ CrCl_3 + 2\ KCl + 7\ H_2O + 3\ S\downarrow \quad (137)$$

The oxidizing action of nitrate ion is somewhat similar to that of dichromate ion. Nitrate ion can break up in the presence of hydrogen ion to give water and an oxide of nitrogen.

$$NO_3^- + 4\ H^+ + 3\ (-) \rightarrow NO + 2\ H_2O \quad (138)$$

$$NO_3^- + 2\ H^+ + (-) \rightarrow NO_2 + H_2O \quad (139)$$

In general, when nitric acid is present in excess and when it is dilute, the reaction will proceed according to Equation 138. When the acid is concentrated, the reaction will proceed according to Equation 139. Under some conditions the nitrate ion can be reduced to ammonia.

The electrons in Equations 138 or 139 might be supplied by a metal, by sulfide ion, or by a metal sulfide as in the dissolving of the metal sulfides of the copper group. In the latter case, for example, sulfur is precipitated and the metal ion is formed.

$$CuS \rightarrow Cu^{++} + S\downarrow + 2\ (-) \quad (140)$$

Equations 138 and 140 can be combined.

$$2\ NO_3^- + 8\ H^+ + 3\ CuS \rightarrow 2\ NO + 4\ H_2O + 3\ Cu^{++} + 3\ S\downarrow \quad (141)$$

This is easily converted into the molecular form. If 6 nitrate ions are added to each side of the equation, the positive and negative ions can be united to give the molecular equation.

$$8\ HNO_3 + 3\ CuS \rightarrow 2\ NO + 4\ H_2O + 3\ Cu(NO_3)_2 + 3\ S\downarrow \quad (142)$$

The oxidizing action of sodium peroxide may appear to be a little different from the cases considered so far. When sodium peroxide acts as an oxidizing agent in water solution, sodium hydroxide is one of the products. Sodium hydroxide consists of sodium ions and hydroxide ions. We may write the partial equation without inquiring how sodium peroxide ionizes.

$$Na_2O_2 + 2\ H_2O \rightarrow 2\ Na^+ + 4\ OH^- \qquad (143)$$

This equation is still unbalanced with respect to charges. As it is written there are on the right side of the equation $4 - 2 = 2$ extra negative charges, and none on the left. To balance them two electrons must be added to the left side.

$$Na_2O_2 + 2\ H_2O + 2\ (-) \rightarrow 2\ Na^+ + 4\ OH^- \qquad (144)$$

Let us assume that manganous hydroxide is the substance being oxidized, as in the separation of manganese and iron ions from aluminum and chromium ions in the analysis of the ammonium sulfide group.

$$Mn(OH)_2 + 2\ OH^- \rightarrow MnO_2 + 2\ H_2O + 2\ (-) \qquad (145)$$

These two partial equations can then be combined to give the complete molecular equation.

There is no definite set of rules to be given to cover the balancing of all kinds of oxidation-reduction equations. Variations in the method of balancing a single equation are possible. Most of the equations encountered in qualitative analysis will be similar to one or another of the examples given and can be worked out in a similar manner.

QUESTIONS

1. Combine Equations 144 and 145, and obtain the molecular equation.
2. Balance the following partial equations:

   (*a*) $Bi^{+++} + (-) \rightarrow Bi$
   (*b*) $Cl_2 + (-) \rightarrow Cl^-$
   (*c*) $Bi_2S_3 \rightarrow Bi^{+++} + S + (-)$
   (*d*) $BiO_3^- + H^+ + (-) \rightarrow Bi^{+++} + H_2O$
   (*e*) $Mn^{++} + H_2O \rightarrow H^+ + MnO_4^- + (-)$
   (*f*) $SnO_2^{--} + OH^- \rightarrow SnO_3^{--} + H_2O + (-)$

3. Name all the substances the formulas for which appear in the equations of Question 2.
4. Write complete molecular equations for the reaction of each of the following pairs of substances. Although some of the equations can be written by inspection, it is suggested that they be worked out by means of partial equations for the practice.

   $BiCl_3 + Zn \rightarrow$
   $SbCl_3 + Fe \rightarrow$
   $CuSO_4 + Zn \rightarrow$
   $Cu + HNO_3 \rightarrow$
   $Bi_2S_3 + HNO_3 \rightarrow$
   $Bi(OH)_3 + Na_2SnO_2 \rightarrow$
   $FeCl_2 + Cl_2 \rightarrow$
   $Fe(OH)_2 + Na_2O_2 + H_2O \rightarrow$
   $Mn(NO_3)_2 + NaBiO_3 + HNO_3 \rightarrow$
   $Bi + Cl_2 \rightarrow$

5. Select from Question 4 the reactions which you have carried out in qualitative analysis and tell where in the scheme each one occurs.

6. What would a precipitate of nothing but sulfur in the hydrogen sulfide group mean?

7. In the test for mercuric ion with stannous chloride, which substance is oxidized and which reduced?

8. When iron is wet with water and rubbed with a crystal of copper sulfate it is copper plated. How can this be explained?

9. Early chemists observed that if an iron vessel was kept for several hours in the water of a certain spring it would turn to copper. How can this observation be explained?

APPENDIX

I. PREPARATIONS OF REAGENTS AND SOLUTIONS

A. Reagents Needed in the Experimental Work of This Book [1]

Acid Acetic, $HC_2H_3O_2$, 6 *M*. Mix 370 cc. of the 99.5% acid with 630 cc. of water.

Acid Fluosilicic (Hydrofluosilicic), H_2SiF_6, 0.5 *M*. Mix 200 cc. of the 27% acid with 800 cc. of water.

Acid Hydrochloric, HCl, 12 *M*. Use the c.p. acid of commerce, density 1.19.

Acid Hydrochloric, 6 *M*. Mix equal volumes of the 12 *M* acid and water.

Acid Nitric, HNO_3, 16 *M*. Use the c.p. acid of commerce, density 1.4.

Acid Nitric, 6 *M*. Mix 380 cc. of 16 *M* acid with 620 cc. of water.

Acid Perchloric, $HClO_4$, 6 *M*. Mix 667 cc. of the 60% acid of commerce with 333 cc. of water.

Acid Sulfuric, H_2SO_4, 18 *M*. Use the c.p. acid of commerce, density 1.84, without dilution.

Acid Sulfuric, 3 *M*. Add 167 cc. of the 18 *M* acid to 500 cc. of water and dilute to 1000 cc.

Alcohol, Ethyl (Denatured), C_2H_5OH. Undiluted.

Aluminon, 0.1% solution. Place 1 g. of aurin tricarboxylic acid [2] in 500 cc. of water. While stirring the mixture add small quantities of ammonium hydroxide till the solid has dissolved. Dilute to 1000 cc. with water.

Ammonium Acetate, $NH_4C_2H_3O_2$, 3 *M* or 321 g. per liter.

Ammonium Carbonate, $(NH_4)_2CO_3$ (composition variable), 3 *M* in $(NH_4)_2CO_3$ and 6 *M* in NH_4OH. Dissolve 250 g. ammonium carbonate in 600 cc. of 6 *M* NH_4OH. Add sufficient 6 *M* NH_4OH to make 1000 cc.

Ammonium Hydroxide, NH_4OH, 6 *M*. Mix 400 cc. of the 14 *M*, c.p. solution of commerce (27% NH_3) with 600 cc. of water.

Ammonium Polysulfide, $(NH_4)_2 S_x$. Saturate 200 cc. of 14 *M* NH_4OH with H_2S gas. Keep the mixture cool during the process. After saturation add 200 cc. more of 14 *M* NH_4OH and enough water to make 1000 cc. of solution. Then add 1 g. of powdered sulfur and shake the mixture thoroughly. Allow the mixture to stand 24 hours or longer before using.

[1] Materials for unknowns not included.

[2] This reagent may be purchased from the Eastman Kodak Company, Rochester, N. Y. or from other sources.

Antimonous Chloride, $SbCl_3$, 0.3 *M*. Dissolve 67 g. in 500 cc. of 6 *M* HCl. Dilute to 1000 cc. with water.

Arsenious Chloride, $AsCl_3$, 0.3 *M*. Dissolve 35 g. As_2O_3 in 200 cc. of 12 *M* HCl. Dilute to 1000 cc. with water.

Asbestos, long fiber, washed in acid. Mix about 15 volumes of water with one volume of fiber.

Barium Chloride, $BaCl_2.2H_2O$, 0.5 *M* or 122 g. per liter.

Barium Hydroxide, $Ba(OH)_2.8H_2O$, 0.2 *M* or 60 g. per liter (saturated solution).

Copper Nitrate, $Cu(NO_3)_2.3H_2O$, 0.5 *M* or 120 g. per liter.

Dimethyl-glyoxime, 0.6% solution. Dissolve 6 g. in denatured ethyl alcohol. Dilute to 1000 cc. with denatured alcohol.

Ferrous Sulfate, $FeSO_4.7H_2O$, 0.5 *M*. Dissolve 138 g. in a mixture of 50 cc. of 6 *M* H_2SO_4 and 450 cc. of water. Dilute to 1000 cc. with water. Keep the solution acid with H_2SO_4 and keep a small piece of iron in the solution to keep the iron in the ferrous state.

Ferrous Sulfide, FeS. Solid, in pieces about 5 mm. diameter.

Hydrogen Peroxide, H_2O_2, 0.3 *M*. Use undiluted the U.S.P. (3%) solution of commerce.

Hydrogen sulfide, H_2S, gas.

Iron, Fe, nails, about 6 d.

Iron, granulated, pieces 1 mm. in diameter. Much latitude in size of pieces is admissible. Cast iron drillings do very well. Avoid extremely fine powders.

Lead Nitrate, $Pb(NO_3)_2$, 0.5 *M* or 165 g. per liter.

Litmus Paper. Part of apparatus outfit.

Mercuric Chloride, $HgCl_2$, 0.25 *M* or 67 g. per liter.

Mercurous Nitrate, $HgNO_3.H_2O$, 0.5 *M*. Dissolve 140 g. in 200 cc. 16 *M* HNO_3. Dilute to 1000 cc. with water. Keep a globule of mercury in the solution.

Nitroso-R-Salt,[1] **0.5%** solution or 5 g. per liter.

Potassium Chlorate, $KClO_3$. Powdered.

Potassium Chromate, K_2CrO_4, 0.5 *M* or 97 g. per liter.

Potassium Ferrocyanide, $K_4Fe(CN)_6$, 0.3 *M* or 140 g. per liter.

Potassium Nitrate, KNO_3. Powdered.

Potassium Oxalate, $K_2C_2O_4.H_2O$, 1.5 *M* or 276 g. per liter.

Practice Solutions. See p. 149.

Silver Nitrate, $AgNO_3$, 0.2 *M* or 34 g. per liter.

Sodium Acetate, $NaC_2H_3O_2.3H_2O$, 3 *M* or 408 g. per liter.

Sodium Bismuthate, $NaBiO_3$, powder. (The commercial product frequently contains both $NaBiO_3$ and Bi_2O_4.)

Sodium Carbonate, Na_2CO_3, anhydrous powder.

Sodium Carbonate, 1.5 *M* or 160 g. of the anhydrous salt per liter.

Sodium Hydroxide, NaOH, 6 *M*. Dissolve 250 g. in 250 cc. water in a porcelain dish, cool and dilute to 1000 cc.

Sodium Peroxide, Na_2O_2, powder.

Sodium Phosphate, $Na_2HPO_4.12H_2O$, 0.3 *M* or 107 g. per liter.

[1] See footnote 2, p. 143.

Stannous Chloride, $SnCl_2.2H_2O$, 0.5 *M*. Dissolve 112 g. in 100 cc. 12 *M* HCl. Dilute to 1000 cc. with water. Keep a small piece of metallic tin in the solution.

B. Solutions Containing Ions in the Scheme of Analysis not Included in A [1]

Aluminum Nitrate, $Al(NO_3)_3.9H_2O$, 0.5 *M* or 180 g. per liter.
Ammonium Chloride, NH_4Cl, 0.5 *M* or 27 g. per liter.
Bismuth Nitrate, $Bi(NO_3)_3.5H_2O$, 0.2 *M*. Dissolve 97 g. $Bi(NO_3)_3.5H_2O$ or 61 g. of $BiONO_3.H_2O$ in 100 cc. of 16 *M* HNO_3. Dilute to 1000 cc. If turbidity appears add more acid.
Cadmium Nitrate, $Cd(NO_3)_2.4H_2O$, 0.5 *M* or 155 g. per liter.
Calcium Chloride, $CaCl_2$, 0.5 *M* or 55 g. per liter.
Chromium Chloride, 0.3 *M*. 32 g. $Cr(OH)_3$ in 55 cc. 6 *M* HCl. Dilute to 1000 cc. with water. Filter if necessary. The solution is prepared by dissolving the hydroxide in acid because chromium chloride salt is deliquescent and hard to manipulate.
Cobalt Nitrate, $Co(NO_3)_2.6H_2O$, 0.3 *M* or 88 g. per liter.
Ferric Chloride, $FeCl_3.6H_2O$, 0.5 *M*. Dissolve 135 g. in a mixture of 25 cc. of 6 *M* HCl and 975 cc. water.
Magnesium Nitrate, $Mg(NO_3)_2.6H_2O$, 0.5 *M* or 128 g. per liter.
Manganese Nitrate, $Mn(NO_3)_2.xH_2O$, 0.5 *M* or about 150 g. per liter.
Nickel Nitrate, $Ni(NO_3)_2.6H_2O$, 0.5 *M* or 145 g. per liter.
Zinc Nitrate, $Zn(NO_3)_2.6H_2O$, 0.5 *M* or 150 g. per liter.

[1] These solutions are not required as reagents but are often convenient for reference.

II. APPARATUS AND MATERIALS

Apparatus and Materials Needed for General Laboratory Use

Distilled water.

Ring stands.

A balance or scale that will weigh from 1 to 50 grams preferably without the use of brass weights.

Paper about 4 inches wide on a roll is convenient for weighing out powders and conveying them to the desk.

Waste jars of stoneware.

Hydrogen sulfide.

The most nearly satisfactory source of hydrogen sulfide is that purchased compressed in cylinders from commercial sources. (The Matheson Co., North Bergen, New Jersey and others.) The gas is transferred from the cylinder to a floating gas holder, similar to the gas holders used for the storage of city gas supplies. From the gas holder the hydrogen sulfide is conducted to suitable outlets in the laboratory.

For small classes a Kipp generator will do, but this is frequently unsatisfactory. For laboratories that produce their own hydrogen sulfide many types of apparatus are available. The Parsons generator, which can be obtained from supply houses is about as satisfactory as any of these. Most generators will do well enough if given sufficient attention, but in practice the attention is not available at critical times.

Nickel or iron crucibles of about 30 cc. capacity. Nickel crucibles are more satisfactory as less metal disintegrates during fusion than with iron. Iron crucibles are cheaper but withstand fewer fusions. "Domes of Silence," hemispherical vessels of sheet iron that may be purchased at most furniture stores for about one cent each may be used for fusions.

Meker burners, Fisher burners, or blast lamps may be used in making fusions. Blast lamps, if improperly regulated may destroy iron or nickel crucibles.

Clay crucibles, bottomless, are helpful in lessening the time for fusions. Secure clay assay crucibles, about three inches in diameter at the larger end and about five inches in height. To make them bottomless requires two persons. One holds the crucible in his hand in an upright position. The other places the cutting end of a cold chisel against the inside bottom of the crucible. By striking the upper end of the cold chisel a vigorous blow with a hammer the crucible is rendered bottomless.

Apparatus Needed for Each Student Desk

Glassware

3 Beakers, each 250 cc.
2 Wide mouthed bottles each to take No. 6 rubber stopper.
4 Erlenmeyer flasks, each 250 cc.
2 Funnels, each about 6.5 cm. diameter.
1 Graduated cylinder, 10 cc.
1 Graduated cylinder, 50 cc.
1 Florence flask, 500 or 1000 cc.
1 Filter flask, side arm, 250 cc.
12 Test tubes, either $\frac{5}{8}$ by 6 or $\frac{3}{4}$ by 7 inches.
1 Watch glass, 4 in. diameter.

Porcelain Ware

1 Casserole, 75 cc.
1 Funnel, Hirsch No. 00.
1 Mortar (70 mm.) and pestle.
1 Evaporating dish, 8 cm. diameter.

Other Apparatus

1 Burner and connection.
1 Fishtail burner tip.
1 Suction pump.
1 Triangle, nichrome or clay.
1 Iron ring, $2\frac{1}{2}$ in. inside diameter.
1 Test tube stand.
1 Test tube holder, wire.
1 Iron tongs.
1 Triangular file.
1 Package filter paper, 10 cm. diameter.
1 Package filter paper, 5 cm. diameter, to fit Hirsch funnel No. 00.[1]
5 ft. glass tubing, 6 mm. external diameter.
6 inches pure gum tubing, $\frac{3}{16}$ inch inside diameter.
1 Sponge.
Red and blue litmus paper in glass containers.
1 Test tube brush.
1 Towel.
1 Wire gauze.

1 Piece white or red rubber tubing $\frac{3}{16}$ inch internal diameter, 30 inches long to connect filter flask with trap and trap with suction.
2 No. 6 rubber stoppers, 1 hole.
1 No. 6 rubber stopper, 2 holes.
1 No. 6 rubber stopper, with no holes.

Pyrex flasks of the kinds included in this list all take about the same sized rubber stoppers, about No. 6, but the openings vary somewhat so that at

[1] Hardened filter paper to fit the Hirsch funnel should be available also.

times a No. 5 or occasionally a No. 7 fits better. In the case of the stopper for the filter flask it is best to purchase No. 6 stoppers without holes and then cut the hole to meet the needs of the porcelain funnel used. By cutting the hole somewhat smaller than the outside diameter of the funnel stem a No. 6 stopper will stretch so as to close the opening in a 250 cc. side arm filter flask. A No. 7 stopper is usually too large for the filter flask and a No. 6 unless cut as just mentioned is too small. The inlet tubes for gas burners vary somewhat in diameter but tubing $\frac{1}{4}$ or $\frac{5}{16}$ inches internal diameter will usually serve the purpose of gas connection.

III. THE PREPARATION OF PRACTICE SOLUTIONS

The authors have not succeeded in preparing a practice solution which would contain all of the metallic ions in the scheme of analysis, without having considerable precipitate form. They have succeeded in preparing two different solutions that were fairly stable for two months or longer and which held in solution 19 different metallic ions. One of these solutions hereafter called the "chloride solution" contains all the metallic ions except those of the hydrochloric acid group, while the second one called the "nitrate solution" contains all the metallic ions except those of the tin group. By further omissions of one or more ions from these solutions practice solutions which vary in composition may be provided in considerable numbers.

Preparation of the chloride solution. To prepare two liters of this solution weigh out the indicated quantities of the following materials and dissolve them in a mixture of 400 cc. of 6 *M* hydrochloric acid and 400 cc. of water. Heating may aid. A small undissolved residue will do no harm.

25 g. $SbCl_3$
10 g. As_2O_3
30 g. $BiCl_3$
15 g. $CrCl_3.xH_2O$
35 g. $SnCl_4.5H_2O$

Weigh out the following and dissolve in a mixture of 400 cc. of 6 *M* hydrochloric acid and 800 cc. of water:

35 g. $AlCl_3.6H_2O(Al_2Cl_6.12H_2O)$
40 g. $BaCl_2.2H_2O$
20 g. $CdCl_2.2H_2O$
40 g. $CaCl_2$ (anhydrous)
20 g. $CoCl_2.3H_2O$
20 g. $CuCl_2.2H_2O$
20 g. $FeCl_3.6H_2O$
40 g. $MgCl_2.6H_2O$
20 g. $MnCl_2.4H_2O$
20 g. $HgCl_2$
20 g. $NiCl_2.6H_2O$
10 g. KCl
10 g. NaCl
15 g. $ZnCl_2$

When dissolved, combine the two solutions, shake well, allow to stand over night. Filter if necessary.

Preparation of the nitrate solution. To prepare two liters of this solution weigh out the following and dissolve in a mixture of 300 cc. of 6 *M* nitric acid and 100 cc. of water:

40 g. $Bi(NO_3)_3.5H_2O$
30 g. $HgNO_3.2H_2O$
30 g. $Hg(NO_3)_2.2H_2O$

Weigh out the following and dissolve in a mixture of 300 cc. of 6 *M* nitric acid and 1300 cc. of water, heating gently and stirring:

30 g. $Al(NO_3)_3.9H_2O$
40 g. $Ba(NO_3)_2$
30 g. $Cd(NO_3)_2.4H_2O$
40 g. $Ca(NO_3)_2.4H_2O$
20 g. $Cr(NO_3)_3$
30 g. $Co(NO_3)_2.6H_2O$ (or anhydrous)
30 g. $Cu(NO_3)_2.3H_2O$
30 g. $Fe(NO_3)_3.9H_2O$
30 g. $Pb(NO_3)_2$
50 g. $Mg(NO_3)_2.6H_2O$
30 g. $Mn(NO_3)_2.xH_2O$
30 g. $Ni(NO_3)_2.6H_2O$
20 g. KNO_3
15 g. $AgNO_3$
20 g. $NaNO_3$
20 g. $Zn(NO_3)_2.6H_2O$

Combine the two solutions, shake thoroughly, allow to stand over night. Filter if necessary.

IV. THE PREPARATION OF SOLID UNKNOWNS

The preparation of solid unknowns that will neither cake nor decompose in storage is an art that requires a wide knowledge of the individual properties of substances. The following suggestions will be helpful in many cases.

For the metallic ions the following are in many cases satisfactory sources: the finely divided metal, the metallic oxides, the chlorides, the nitrates, the carbonates, or the sulfates.

For negative ions, the sodium or potassium salts are usually satisfactory sources.

In general avoid the mixing of deliquescent salts or substances which if placed in water solution would react with each other or with water to form a precipitate or a volatile compound.

Salts that are extremely soluble at ordinary temperatures or that have a large quantity of water of hydration per molecule are more often deliquescent than otherwise.

The following are a few of the specific combinations to be avoided: chlorides with silver, lead or mercurous mercury; nitrates with anything but nitrates; sulfates with silver, lead, mercurous, barium and calcium salts; salts of weak acids with salts of strong acids that hydrolyze, sodium carbonate with copper sulfate for example.

With most solid unknowns a sample having a volume of 10 to 15 cc. is adequate for the needs of an individual student. Small straight sided bottles without necks (homeopathic vials) have been found satisfactory containers of samples for students.

V. THE ATOMIC WEIGHTS OF SOME OF THE MORE COMMON ELEMENTS

[From the Journal of the American Society, 50, 615 (1928).]

Aluminum	Al	26.97	Magnesium	Mg	24.32
Antimony	Sb	121.77	Manganese	Mn	54.93
Arsenic	As	74.96	Mercury	Hg	200.61
Barium	Ba	137.37	Nickel	Ni	58.69
Bismuth	Bi	209.00	Nitrogen	N	14.008
Cadmium	Cd	112.41	Oxygen	O	16.00
Calcium	Ca	40.07	Potassium	K	39.10
Carbon	C	12.00	Silicon	Si	28.06
Chlorine	Cl	35.46	Silver	Ag	107.88
Chromium	Cr	52.01	Sodium	Na	23.00
Cobalt	Co	58.94	Sulfur	S	32.06
Copper	Cu	63.57	Tin	Sn	118.70
Hydrogen	H	1.008	Zinc	Zn	65.38
Iron	Fe	55.84			
Lead	Pb	207.22			

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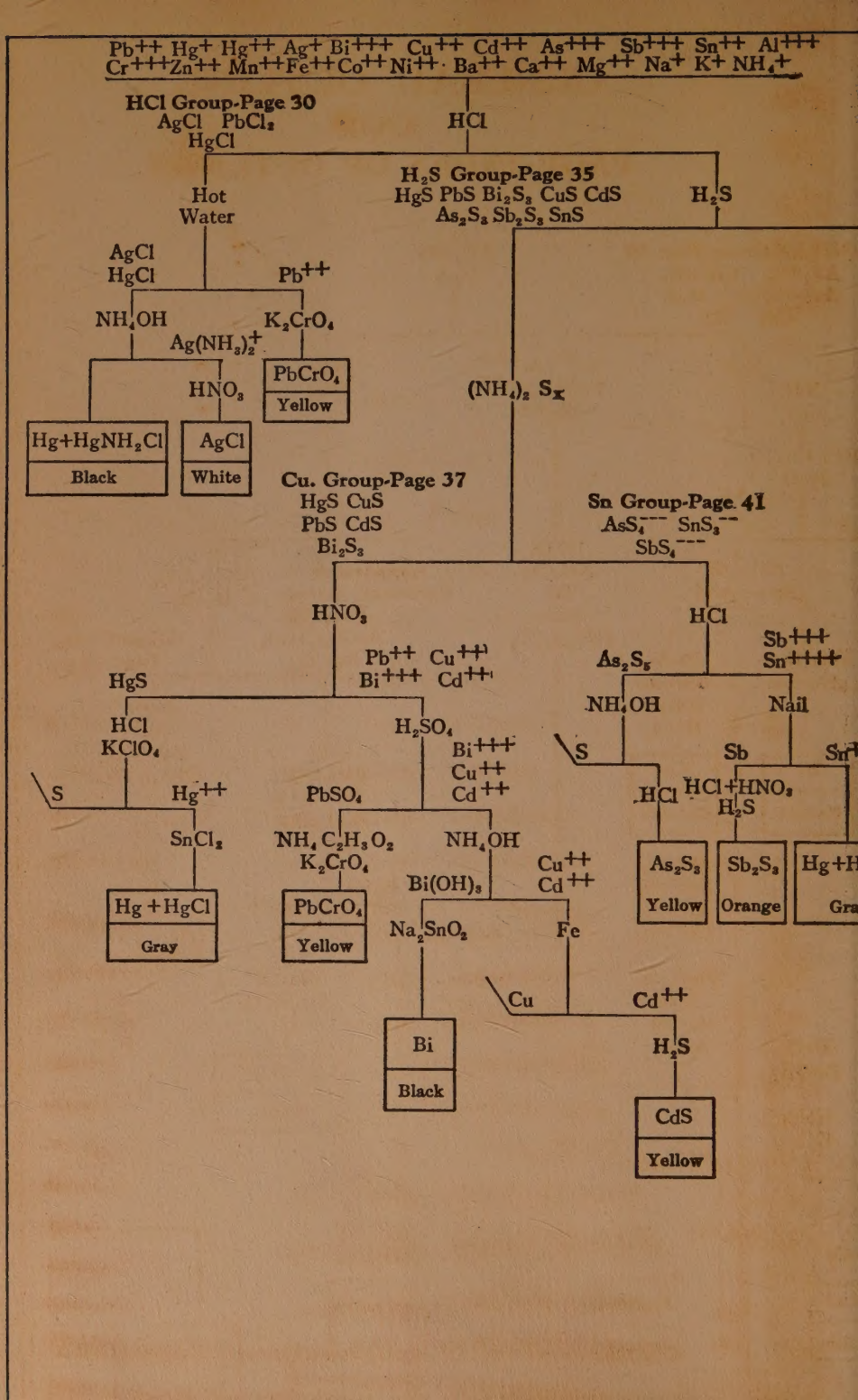
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Cr+++ Zn++ Mn++ Fe++ Co++ Ni++ Ba++ Ca++ Mg++ Na+ K+ NH4+
HCl Group-Page 30
AgCl PbCl2
HgCl
HCl
H2S Group-Page 35
HgS PbS Bi2S3 CuS CdS
As2S3 Sb2S3 SnS
H2S
Hot
Water
AgCl
HgCl
Pb++
NH4OH
K2CrO4
Ag(NH3)2+
PbCrO4
Yellow
HNO3
Hg+HgNH2Cl
Black
AgCl
White
(NH4)2 Sx
Cu. Group-Page 37
HgS CuS
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Bi2S3
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AsS4--- SnS3--
SbS4---
HNO3
HCl
Pb++ Cu++
Bi+++ Cd++
As2S5
Sb+++
Sn++++
HgS
NH4OH
Nail
HCl
KClO4
H2SO4
Bi+++
Cu++
Cd++
S
Hg++
PbSO4
S
Sb
Sn
HCl
HCl+HNO3
H2S
SnCl2
NH4C2H3O2
K2CrO4
NH4OH
Cu++
Cd++
Bi(OH)3
As2S3
Yellow
Sb2S3
Orange
Hg+H
Gra
Hg+HgCl
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PbCrO4
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